PB87-133112

PCB (Polychlorinated Biphenyl) Sediment Decontamination - Technical/Economic Assessment of Selected Alternative Treatments

Research Triangle Inst.
Research Triangle Park, NC

Prepared for

Environmental Protection Agency, Cincinnati, OH

Dec 86

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/2-86/112	2.	3. RECIPIENT'S ACCESSION NO. PB87 133112/AS
4. TITLE AND SUBTITLE PCB SEDIMENT DECONTAMINATION - TECHNICAL/ECONOMIC ASSESSMENT OF SELECTED ALTERNATIVE TREATMENTS		5. REPORT DATE December 1986 6. PERFORMING ORGANIZATION CODE Research Triangle Institute
7. AUTHOR(S) Ben H. Carpenter		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute P. O. Box 12194 Research Triangle Park, NC 27709		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Hazardous Waste Engineering Research Laboratory Office of Research and Development U. S. Environmental Protection Agency Cincinnati, OH 45268		13. TYPE OF REPORT AND PERIOD COVERED Final - 6/85-2/86 14. SPONSORING AGENCY CODE EPA/600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Eleven emerging alternative treatments for PCB-contaminated sediments have been compared and ranked using technical performance, status of development, test and evaluation data needs, and cost as factors. In ranking the processes, weights were assigned the factors to emphasize the extent of decontamination, the estimated cost of treatment, and the versatility of the process.

The emerging treatment processes represent six of the nine potentially applicable types of technologies: low-temperature oxidation, chlorine removal, pyrolysis, removing and concentration, vitrification, and microorganisms. Types of technologies not developed are chlorinolysis, stabilization, and enzymes.

On the basis of the comparisons made, the treatment processes were ranked in the following order from highest to lowest: KPEG, LARC, Acurex, Bio-Clean, Supercritical Water, Advanced Electric Reactor, Vitrification, OHM Extraction, Soilex, Composting, and Sybron Bi-Chem 1006. The first eight processes show potential for reduction of PCB concentrations to the desired background levels (1 to 5 ppm) or less, with minimum environmental impacts and low to moderate cost. All the technologies except the advanced electric reactor require further development and testing.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO THE PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 134
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

PB87-133112

EPA/600/2-86/112
December 1986

PCB SEDIMENT DECONTAMINATION-TECHNICAL/ECONOMIC ASSESSMENT OF SELECTED ALTERNATIVE TREATMENTS

by

Ben H. Carpenter
Research Triangle Institute
Research Triangle Park, North Carolina 27709

Contract No. 68-02-3992
RTI Project No. 471U-3065-26

Project Officer

Donald L. Wilson
Hazardous Waste Engineering Research Laboratory
Cincinnati, Ohio 45268

HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

NOTICE

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract No. 68-02-3992 to the Research Triangle Institute. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsiblities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes eleven emerging treatment processes that show potential for decontaminating Polychlorinated Biphenyl (PCB)-contaminated sediments. The comparisons of these processes in terms of technical performance, status of development, test and evaluation data needs, and estimated cost of application should be useful to EPA Regional Offices, to those concerned with developing hazardous waste treatment regulations, and to those interested in the development of new and innovative treatments.

For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser, Director
Hazardous Waste Engineering Research
Laboratory

ABSTRACT

Eleven emerging alternative treatments for PCB-contaminated sediments have been compared and ranked using technical performance, status of development, test and evaluation data needs, and cost as factors. In ranking the processes, weights were assigned the factors to emphasize the extent of decontamination, the estimated cost of treatment, and the versatility of the process.

The emerging treatment processes represent six of the nine potentially applicable types of technologies: low-temperature oxidation, chlorine removal, pyrolysis, removing and concentration, vitrification, and microorganisms. Types of technologies not developed are chlorinolysis, stabilization, and enzymes.

On the basis of the comparisons made, the treatment processes were ranked in the following order from highest to lowest: KPEG, LARC, Acurex, Bio-Clean, Supercritical Water, Advanced Electric Reactor, Vitrification, OHM Extraction, Soilex, Composting, and Sybron Bi-Chem 1006. The first eight processes show potential for reduction of PCB concentrations to the desired background levels (1 to 5 ppm) or less, with minimum environmental impacts and low to moderate cost. All the technologies except the advanced electric reactor require further development and testing.

This report was submitted in fulfillment of Contract No. 68-02-3992 Task 26 by Research Triangle Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from June 1985 to February 1986, and work was completed as of March 1986.

CONTENTS

Section Page

Notice ii
Foreword iii
Abstract iv
Figures vii
Tables ix
Abbreviations and Symbols x
Acknowledgments xii

1 Introduction 1
  1.1 Background 1
  1.2 Purpose 1
  1.3 Approach 2
    1.3.1 Data Acquisition 2
    1.3.2 Screening and Selection of Most Technically Feasible Processes 2
    1.3.3 Development of Criteria 3
    1.3.4 Process Assessment 3
  1.4 Scope of the Report 4

2 Conclusions 5

3 Screening of Alternative Treatment Processes 7

4 Development of Evaluation Criteria 12
  4.1 Problem Definition 12
  4.2 Regulatory Factors 12
  4.3 Technical Factors 13
    4.3.1 Residual PCB Consideration in Treated Sediments 14
    4.3.2 Available Capacity 14
    4.3.3 Conditions/Limitations 14
    4.3.4 Concentration Range Handled 14
    4.3.5 Status of Development 14
    4.3.6 Test and Evaluation Data Needs 15
    4.3.7 Unit Operations 15
    4.3.8 Estimated Costs 15
  4.4 Cost Estimates 15
    4.4.1 Cost Estimation Methodology 15
    4.4.2 Baseline Cost Estimate 19
    4.4.3 Incineration Cost Estimate 19
    4.4.4 Alternative Treatment Cost Estimate 19

CONTENTS (continued)

Section Page

5 Assessment of Alternative Treatment Processes 20
5.1 Processes Based on Chemical Technologies 20
5.1.1 Supercritical Water Oxidation 20
5.1.1.1 Principles 20
5.1.1.2 Modar SCW Process 21
5.1.2 Nucleophilic Substitution 24
5.1.2.1 Principles 24
5.1.2.2 KPEG Terraclean-Cl Process 26
5.1.3 Radiant Energy-Ultraviolet Light 38
5.1.3.1 Principles 38
5.1.3.2 LARC Process 39
5.1.4 Pyrolysis 46
5.1.4.1 Prinicple 46
5.1.4.2 Advanced Electric Reactor, J. M. Huber Corporation 46
5.1.5 Thionation 53
5.2 Processes Based on Physical Technologies 54
5.2.1 Extraction 54
5.2.1.1 Principles 54
5.2.1.2 Acurex Solvent Wash Process 56
5.2.1.3 O.H. Materials Methanol Extraction Process 60
5.2.1.4 Soilex Solvent Extraction Process 63
5.2.2 Vitrification 67
5.2.2.1 Principles 67
5.2.2.2 Battelle In Situ Vitrification Process 67
5.3 Biological Technologies 71
5.3.1 Microorganisms and Enzymes 71
5.3.1.1 Principles 71
5.3.1.2 Indigenous and Conventional Chemical Mutants 72
5.3.1.3 Enzyme Mechanisms 77
5.3.1.4 Bio-Clean Process 78
5.3.1.5 Sybron Bi-Chem 1006 PB/Hudson River Isolates Process 81
5.3.1.6 Composting 83
5.4 Supporting Processes 84
5.4.1 Dredging 85
5.4.1.1 Classes of Dredge 85
5.4.1.2 Dredge System Evaluation 88
5.4.2 Wastewater Treatment Methods 91
5.4.2.1 Mechanical Removal 91
5.4.2.2 Activated Sludge 91
5.4.2.3 Trickling Filter 92
5.4.2.4 Special Biological Treatment Processes 92
5.4.2.5 UV/Ozonation 93
5.4.2.6 Carbon Adsorption................... 93

CONTENTS (Continued)

Section Page

6 Characterization and Ranking of Alternative Treatment Processes 95
6.1 Characterization 95
6.2 Ranking of Treatment Processes 98
6.2.1 Residual PCB Concentration in Treated Sediments 102
6.2.2 Available Capacity 102
6.2.3 Conditions/Limitations 102
6.2.4 Concentration Range Handled 103
6.2.5 Status of Development 103
6.2.6 Test and Evaluation Data Needs 103
6.2.7 Estimated Costs 104
6.2.8 Overall Ranking 104

7 Bibliography 107

FIGURES

Number Page

1 Schematic of the Modar SCW oxidation process 22
2 Schematic of KPEG process 28
3 Schematic of scaled-up KPEG process 31
4 Schematic of dioxin-treatment system 32
5 Schematic of single-lamp LARC reactor 40
6 LARC degradation of Aroclor 1260 in basic isopropanol 43
7 Schematic of LARC mobile unit for destruction of PCB's in soil 45
8 Vertical cross section of the Advanced Electric Reactor 47
9 Schematic of Advanced Electric Reactor process 49
10 Schematic of Acurex solvent wash process 59
11 Conceptual flow sheet, methanol extraction of PCB's from discussion with Robert Caron, EPA, Philadelphia regional office 61
12 Soilex pilot plant 64
13 Soilex steam distillation unit 66
14 Engineering scale vitrification system and sample locations 69
15 Bio-Clean process applied to contaminated soils 80
16 Alternative treatment costs, PCB D/D/R processes 101

TABLES

Number		Page
1	Screening of PCB Treatment Processes	8
2	Unit Cost Estimates for Steps Involved in Treatment and Disposal of PCB-Contaminated Sediments	18
3	Extraction Data for Chlorinated Organics from Soil	42
4	Extraction of PCB's from Soil, Effect of Tween	55
5	Results of Soil Cleaning Tests, Acurex Solvent Washing Process	57
6	PCB Degradation by Bacterial Strains: Percent Degradation by Cogener (Rapid Assay Test)	74
7	PCB Degradation by Bacterial and Fungal Strains: Longer Tests	75
8	Dredge Evaluation Matrix; Spill Scenario: Land and Nonnavigable Waters--All Spill Sizes	89
9	Dredge Evaluation Matrix; Spill Scenario: Rivers--All Spill Sizes	90
10	Treatment Process Assessment	96
11	Treatment Process Assessment	99
12	Ranking of Emerging Treatments for PCB-Contaminated Sediments	106

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AER -- Advanced Electric Reactor
ATP -- Adenosine triphosphate
CFR -- Code of Federal Regulations
COD -- chemical oxygen demand
CWO -- catalyzed wet oxidation
D/D/R -- destruction/detoxification/removal
DE -- destruction efficiency
DMSO -- dimethyl sulfoxide
DNA -- deoxyribonucleic acid
ISV -- in situ vitrification
kcal -- kilocalorie
KPEG -- potassium poly(ethylene glycolate)
%CV's -- percent coefficients of variability
MT -- metric ton
PCB(s) -- polychlorinated biphenyl(s)
PEG -- poly (ethylene glycol)
PEGM -- poly (ethylene glycol methyl ether)
PRTZ -- post-reactor treatment zones
RCRA -- Resource Conservation and Recovery Act
scfm -- standard cubic feet per minute
SCM -- standard cubic meter
TSCA -- Toxic Substances Control Act
UV -- ultraviolet

SYMBOLS

Å -- angstrom
atm -- atmosphere
CCl_4 -- carbon tetrachloride
d -- day
g -- gram
g/L -- grams per liter
h -- hour
HCl -- hydrogen chloride
kWh -- kilowatt hour
m -- meter
m^2 -- square meter
Mg -- megagrams
mg/L -- milligrams per liter
min -- minute
nm -- nanometer
pd -- palladium
ppb -- parts per billion
ppm -- parts per million
ppt -- parts per trillion
ug/mL -- micrograms per milliliter
V -- volt
wk -- week
-- pound
g/mL -- grams per milliliter

METRIC CONVERSIONS

1 gal = 3.785 L
1 lb = 0.4536 kg
1 yd^3 = 0.7646 m^3

ACKNOWLEDGMENTS

The contributions, guidance, and advice provided by the EPA Technical Project Manager, Donald L. Wilson, and by Charles J. Rogers, Chief, Chemical and Biological Staff, are gratefully acknowledged. At RTI, the study was conducted under the supervision of Dr. Forest O. Mixon, Jr., Vice President, Chemical Engineering. Ms. Coleen M. Northeim conducted the literature search. Several proponents of emerging technologies provided descriptions, test data, and cost estimates for their developing PCB treatments, which are presented in the ranking and evaluation sections of this report. Their contributions are also gratefully acknowledged and are referenced throughout the report.

SECTION 1
INTRODUCTION

1.1 BACKGROUND

The PCB contamination problems in New Bedford, Massachusetts, the Hudson River in New York, and in Waukegan, Illinois, are reported to be the worst in the United States in terms of concentration and total quantity of PCBs. Also, there are numerous industrial lagoons contaminated with large quantities of PCBs. Dredging to decontaminate harbors/rivers and lagoons is only a partial solution to the problems until effective disposal/treatment methods for dredged PCB-contaminated sediments become available.

The EPA Regional Offices have been asked to comment on the technical and economic feasibility of processes proposed for the cleanup of these sediments and sludges. The Regional Offices do not have adequate data to recommend any specific process from a number of processes currently being proposed or tested/evaluated for the removal of PCBs from contaminated sediments.

1.2 PURPOSE

This study was undertaken for three main reasons: to identify the most technically feasible processes that have been proposed by research concerns for the removal of PCBs from sediments; to identify their extent of development, effectiveness, limitations, and probable costs; and to compile a report describing the technical and economic data available on such processes. The primary objective was to identify the most promising process(es) and to determine needs for further development.

This is the first phase of three phases of study. Future phase two will deal with the evaluation of the unit operations involved in the processes, examine them further against engineering, health, and environmental criteria, and recommend three of them for further testing and evaluation. Phase three will address a definitive assessment of these alternative treatment processes using bench or pilot systems and representative contaminated sediments. Ongoing related work by the EPA Technical Evaluation Staff at Edison, New Jersey is addressing the adaptation of existing commercial extraction technologies to removal of contaminants from solids (soils, sediments, etc.), the characterization of superfund site contamination, and pilot-scale studies of extraction, using water with additives (particulates, chelating, phase-transfer, etc.).

1.3 APPROACH

The study involved four phases: data acquisition, screening and selection of the most technically feasible processes, development of criteria for process assessment, and process assessment.

1.3.1 Data Acquisition

Three major sources of data were EPA's Technical Project Officer, the open literature, and direct contacts with proponents of treatment technologies. EPA's file of proposals and correspondence concerning problems of PCB contamination and possible approaches to alternative solutions proved invaluable in directing the contacts for further information.

A bibliography was prepared, which included approximately 100 references containing information useful in defining potential treatment technologies and in analyzing treatment process performance data. This bibliography was expanded to 171 references by addition of treatment feasibility study reports, process test and evaluation reports, process development proposals, and patents. As processes were identified, direct contacts were made with the investigators for details of their process studies. These contacts are identified throughout the text.

1.3.2 Screening and Selection of Most Technically Feasible Processes

Alternative (non-incineration) destruction/detoxification/removal (D/D/R) processes were subjected to screening to identify those to be assessed further. The processes were categorized according to their generic technology so that appropriate technical screening criteria could be applied for each. This screening yielded 11 emerging processes for further assessment. The selected processes represent six different generic technologies.

1.3.3 Development of Criteria

Criteria used to assess the identified emerging technologies included: residual PCB concentration in treated sediments, available capacity, conditions/limitations (including range of PCB concentration handled), the developmental status, test and evaluation (T and E) data needs, and estimated cost of treatment.

1.3.4 Process Assessment

The assessment of the different processes required consideration of the characteristics inherent in the criteria. Their capability to remove PCBs adequately from wet contaminated sediments, the required processing time, and process controllability were all considered. Available data were examined for limits on the range of PCB concentrations that could be adequately reduced by the process to yield a treated sediment eligible for delisting. The status of development, whether laboratory-scale or pilot-scale, was identified. The extent of available data - whether showing only tests of the concept or lists of the unit processes of a pilot-scale process system - was identified. A preliminary estimate of the cost of applying the process was developed in conjunction with the Developer.

Because the processes identified were at various stages of development, data deficiencies exist, and engineering judgement was used to supplement available information.

Using the information obtained and developed, the characteristics for each process were given subjective ratings relative to an arbitrarily-defined perfect process. These ratings were then weighted and summed to give a single number that could represent the overall relative rating of each process.

1.4 SCOPE OF THE REPORT

Section 3 of this report describes the screening of alternative technologies for technical feasibility to treat PCB-contaminated sediments. Section 4 describes the development of criteria to assess selected processes. Section 5 describes the assessment of the processes, including descriptions, analyses of performance potential, and cost estimates. Section 6 summarizes the characteristics of the selected processes and ranks them subjectively. Section 7 presents a bibliography of references used and other relevant sources. Contacts with developers of the processes are noted throughout the text.

SECTION 2

CONCLUSIONS

Emerging treatment processes for decontamination of PCB-contaminated sediments that show potential as alternatives to incineration and chemical waste landfill have been identified. Eight processes -- KPEG, LARC, Acurex, Bio-Clean, Supercritical Water, Advanced Electric Reactor, Vitrification, and O.H.M. Extraction -- rank highest in terms of potential for cleanup of contaminated sediments. The sediments must be dredged for application of these treatments.

Of the 11 processes assessed, all but the Advanced Electric Reactor (AER) are in various stages of development from laboratory-scale through field tests. The AER is a permitted treatment based on completed trial burns.

There is no immediately available capacity for any of the treatments. Further data are needed in most cases to define the final system design for the process.

At this stage of development, estimated costs of application of the emerging treatments are less than or within the range of the costs of chemical waste landfill, except the AER estimated cost, which exceeds that of landfill but is below the cost of incineration. The ranges of estimated costs (1985 dollars) are as follows:

KPEG	$ 211	to	$ 378/m^3
O.H.M. Methanol Extraction	400	to	514/m^3
Advanced Electric Reactor	830	to	942/m^3
Acurex solvent wash	196	to	569/m^3
Bio-Clean	191	to	370/m^3
Vitrification	255	to	548/m^3
LARC	223	to	336/m^3
Modar supercritical water	250	to	733/m^3
Soilex solvent extraction	856	to	913/m^3
Sybron Bi-Chem 1006 PB	unable to estimate cost		
Composting	unable to estimate cost		
Chemical waste landfill	260	to	490/m^3
Incineration	1,713	to	1,826/m^3

These costs are planning estimates only. In most cases, further research is needed to provide data suitable for more definite cost estimates.

The emerging treatment processes are based on six different technologies: one on low-temperature oxidation, two on chlorine removal, one on pyrolysis, three on removing and concentrating, one on vitrification, and three on microorganisms. Types of generic technologies not yielding competitive emerging processes are: chlorinolysis, stabilizing, and enzymes. A search of these technologies yielded no suitable candidate processes at this time.

SECTION 3

SCREENING OF ALTERNATIVE TREATMENT PROCESSES

This section describes the screening of all processes disclosed in the acquired data to select those to be assessed further as potential alternative treatments for PCB-contaminated sediments. The processes were screened by examining each for any undesirable aspects. Processes with such aspects were rejected from further assessment. For example, lack of tolerance for water by a process is undesirable because of the extensive sediment drying it necessitates. There is evidence in the collected data that such drying generates fine particulates that must be removed from the exit gases of the dryers. The recovered particulates must also be decontaminated. Processes showing insufficient tolerance for water were therefore rejected from further consideration as a primary treatment process in favor of more tolerant alternatives.

Table 1 lists the processes screened, identifies those selected for further assessment, and gives the reasons for rejection of the rest. The processes are arranged according to the generic types of technologies upon which they are based. The use of generic technology types guided the survey and assessment phases of this study by providing technologies from which treatment processes could arise. Some of the technologies (e.g., nucleophilic substitution) have provided several processes. Some (e.g., enzymes) have not yet provided any processes. These technologies are nevertheless discussed to describe their status, with respect to PCB-contaminated sediment treatment, so that their potential may be considered in research planning.

A process rated "1" in Table 1 for each technology has been selected for further assessment and will be discussed in Section 5. Higher rating numbers assigned the rest of the screened processes refer to footnotes that identify the reason for rejection of the process for further assessment.

TABLE 1. SCREENING OF PCB TREATMENT PROCESSES

Generic technology	References	Process	Evaluation[a]
CHEMICAL	Centofanti 1971; Chen 1982; Childs 1982; Craddock 1982; Edwards et al. 1982; Environment Canada 1983; Hornig 1984; Massey and Walsh 1985; Rogers and Kornel 1985; Rogers 1983; Rogers 1985.		
Low-temperature oxidation			
Wet air oxidation	Baillod et al. 1978; Miller and Sevientoniewski (n.d.); Miller and Fox 1982.	Uncatalyzed, general	2
		Zimpro Process, Santa Maria, CA Waste Site	4,13
		Catalyzed	
		Dow Chemical Co. Patent 3,984,311	2
		IT Environmental Science	2
Supercritical water oxidation	Modell et al. 1982.	Modar	1
Chemical oxidants	FMC Corporation (n.d.); March 1968.	Potassium permanganate plus Chromic Acid and Nitric Acid	6
		Chloroiodides	4,7
		Ruthenium tetroxide	3,4,8
Ozonation	Arisman et al. 1981; Lacy and Rice Deschlaeger 1976; Prengle and Mauk 1978.	GE UV/ozonation process	2
Chlorine removal	U.S.P. 346, 636	Molten aluminum/distillation	14
Dehydrochlorination	Chu and Vick 1985; Lapiere et al. 1977.	Catalytic:	2,3
		Nickel on kieselguhr	2,3
		Pd on charcoal	2,3
		Lithium aluminum hydride	2,3
		Butyl lithium	2,3
		Raney Nickel	2,3
Reducing agents	Chu and Vick 1985; Sworzen and Ackerman 1982.	Sodium in liquid ammonia	7,9
		Nickel-catalyzed zinc reduction	7,9
		Hydrazine	7,9
		UV light plus hydrogen	2
		Mildly acidic zinc powder, Sweeney and Fisher (1970)	2,14
Nucleophilic substitution	Brown et al. 1985a; Brunelle and Singleton 1985; March 1968; New York University 1984; Ruzz et al. 1985; Smith and Gurbacham 1981; Sunohio (n.d.); Sweeny and Fischer 1970; United States Patent Office 1984b; Weitzman 1984; Weitzman 1984; Weitzman 1985.	Sodium-based processes:	
		Goodyear, sodium in naphthalene (1980)	10
		Acurex, proprietary solvent	10
		PCBX/Sun Ohio	10
		PPM	10
		Ontario Hydro Power	10

(continued)

TABLE 1 (continued)

Generic technology	References	Process	Evaluation[a]
Nucleophilic substitution (continued)		Potassium poly (ethylene glycolate) based:	
		EPA In-house KPEG	1
		KPEG Terraclean-Cl	1
		GE KOH-PEG	11
		New York University KPEG	12
Radiant energy	Bailin and Hertzler 1977; Bailin and Hertzler 1978; Bailin et al. 1978; Craft et al. 1975; Dev et al. 1985; Kalmaz et al. 1981; Meuser and Weimer 1982; Plimmer 1978; Rogers and Kornel 1985; Rogers 1985; Trump et al. 1979; West et al. 1983.	UV/photolysis	3
		Syntex photolytic	3,4
		Thermal corona glow	5
		Microwave plasma	9,17
		RF insitu heating	18
		Gamma radiation (Craft et al. 1975)	9
		LARC	1
Electromechanical reduction	Massey and Walsh 1985.	Electromechanical research process	14
Chlorinolysis	Sworzen and Ackerman 1982.	Hoechst process	9
		Goodyear catalytic hydrogenolysis	9
		Exhaustive chlorination	9
Pyrolysis	Boyd 1985; New York State Department of Environmental Conservation 1985a; New York State Department of Environmental Conservation 1985b.	Advanced Electric Reactor	1
		Wright-Malta alkaline catalyst fuel-gas process	12
PHYSICAL			
Removing and concentrating	Angiola and Soden 1982; Caron 1985; Gilmer and Freestone 1978; Githens 1984; Hancher et al. 1984; Hawthorne 1982; Lee et al. 1979; Saunders 1985; Schwinn et al. 1984; Versar, Inc. 1984.		
Heated Air Stripping		American Toxics Disposal, Inc.	14
Extraction		Critical Fluid Systems, CO_2	14
		Furfural	15
		Acurex solvent wash	1
		O. H. M. extraction	1
		Soilex process	1
Adsorption		Carbon adsorption, general	13
		Neoprene rubber adsorption	15
Vitrification	Timmerman 1985.	Battelle vitrification process	1

(continued)

TABLE 1 (continued)

Generic technology	References	Process	Evaluation[a]
Stabilizing	Ghassemi and Haro 1985; Law Engineering Testing Company 1982; Stroud et al. 1978; Subnamanian and Mahalingam 1977; Tittlebaum et al. 1985.	Asphalt with lime pretreatment	16
		Z-Impremix	15
		Sulfur-asphalt blends (K-20)	16
		Ground freezing	13
Bottom recovery	Carich and Tofflemire 1983; Hand and Ford 1978; Murakami and Takeishi 1978; U.S. Army Corps of Engineers Water Resources Support Center 1983; Zimmie and Tofflemire 1978.	Dredging	13
BIOLOGICAL			
Microorganisms	Bedard et al. 1985; Bumpus et al. 1985; Clark et al. 1979; Dawes and Sutherland 1976; Furakawa 1982; Isbister et al. 1984; Kong and Sayler 1983; McCormick 1985;	Bio-Clean	1
		Sybron Bi-Chem 1006 PB	1
		Composting	1
		Bio-Surf	4,13
	New York State Department of Environmental Conservation 1985a; New York State Department of Environmental Conservation 1985b; Rhee et al. 1985b; Rhee et al. 1985; Unterman et al. 1985.	Ecolotrol, Inc.	4,13
		Wormes Biochemical's Phenobac	1,13
		Rhee anaerobic degradation	14
Enzymes	Catelani et al. 1971; Rochkind et al. Unterman et al. 1985.	No processes found	

[a] Explanation of process rating:

1. Identified emerging sediment treatment process.
2. Destruction efficiency appears to be too low to meet environmental goals.
3. Processing time appears to be extremely long for practical timely cleanup.
4. Data available for dioxin, other chlorinated compounds, or other contaminants, but not PCB's.
5. Process has been shown to destroy PCB's in gas streams only. It may be feasible for sediments, but has not been shown to be.
6. PCB's with 5-7 chlorine atoms per molecule are not destroyed.
7. Products of partial degradation may be toxic.
8. Reagent is very costly/toxic or both.
9. Process costs appear to be excessively high compared with other emerging treatment processes.

10. Water destroys the reagent or interferes with its action, thus the process would require excessive drying of sediments and, probably, extraction in pretreatments. The process would therefore have application only as a subordinate final step to several extraction and concentration operations.

11. This particular process was not evaluated because data were not available for assessment.

12. This process is an alternative to another process using the same generic technology, but it is in very early stages of development, and data were not available for assessment.

13. This technique is basically applicable to preliminary operations prior to treatment or to treatment of wastestreams (e.g., wastewaters) from chemical or physical treatments.

14. This process is in the concept stage and data are insufficient to assess it for PCB-contaminated sediments.

15. This process has been found to be ineffective.

16. This technology provides only for encapsulation of the PCB-contaminated sediments.

17. This process supports incineration of PCB's.

18. The process does not appear to be feasible for submerged sediments.

SECTION 4

DEVELOPMENT OF EVALUATION CRITERIA

4.1 PROBLEM DEFINITION

The PCB contamination problem in the Hudson River is representative of the type of PCB destruction/detoxification problems focused on in this study. The New York State Department of Environmental Conservation (DEC) recently concluded a 2-year survey of 40 miles of the upper Hudson River (1976-1977). The survey, conducted with consultant Malcolm Pirnie, Inc. (White Plains, New York) identified 40 spots collectively containing more than an estimated 382,000 m^3 (500,000 yd^3) of sediment contaminated with PCBs at concentrations greater than 50 ppm. The depth of contamination seems to be between 0.25 and 0.45 meters. A more recent survey (1984) was made of a 5-mile reach extending downstream 5 miles from Ft. Edward, New York. Samples from the near-shore area showed from 40 to 60 ppm PCBs (M. P. Brown 1985).

A pilot dredging operation, performed with hydraulic dredges between 1978 and 1979, netted 152,900 m^3 (200,000 yd^3) of material with seemingly little dispersion of the contaminant downstream. The contaminated areas are located in shallow, slow-moving waters near the riverbanks.

Although DEC is investigating other disposal methods, it is expected to dredge the contaminated sediments and bury them because of the high costs of alternatives (ENR, January 9, 1986).

The wetness of the sediments will preclude the use of many treatment processes designed to treat PCB-containing oils using reagents that would be destroyed or made ineffective in the presence of water.

4.2 REGULATORY FACTORS

The goal for detoxification/destruction is to have no more than 1 to 5 ppm PCBs in the treated sediment. At present, PCB disposal is regulated under TSCA [40 CFR 761.60 a 5 (i-iii)]:

(5) All dredged materials and municipal sewage treatment sludges that contain PCBs at concentrations of 50 ppm or greater shall be disposed of:

(i) In an incinerator which complies with 761.70,

(ii) In a chemical waste landfill which complies with 761.65*; or

(iii) Upon application, using a disposal method to be approved by the Agency's Regional Administrator in the EPA Region in which the PCBs are located. Applications for disposal in a manner other than prescribed in (i) or (ii) of this section must be made in writing to the Regional Administrator. The application must contain information that, based on technical, environmental, and economic considerations, indicates that disposal in an incinerator or chemical waste landfill is not reasonable and appropriate, and that the alternate disposal method will provide adequate protection to health and the environment. The Regional Administrator may request other information that he or she believes to be necessary for evaluation of the alternate disposal method. Any approval by the Regional Administrator shall be in writing and may contain any appropriate limitations on the approved alternate method for disposal. In addition to these regulations, the Regional Administrator shall consider other applicable Agency guidelines, criteria, and regulations to ensure that the discharges of dredged material and sludges that contain PCBs and other contaminants are adequately controlled to protect the environment. The person to whom such approval is issued must comply with all limitations contained in the approval.

The criterion of 1 to 5 ppm for a promising alternative treatment should result in a treated sediment that is disposable without restriction.

4.3 TECHNICAL FACTORS

Technical factors relate to a broad range of principles of operation of diverse applied technologies. Factors have been chosen that can be used effectively in comparing one treatment process with another. Additional factors, specific to a technology, have been chosen to help portray the inherent strengths and limitations of a process.

---

*The reference CFR 761.65 in 5 (ii) cited above is apparently an error because this part of the regulation covers temporary storage for disposal. Chemical waste landfill compliance requirements are cited as CRF 761.75 in other parts of the regulations.

4.3.1 Residual PCB Concentration in Treated Sediments

The goal set for process performance is to reduce the PCB concentration in treated sediments to background levels of 1 to 5 ppm. Several of the processes were found to meet this goal.

4.3.2 Available Capacity

Available capacity was found not to exist for any of the processes. However, several were developed sufficiently to permit projections of the time required to build a facility for application of the treatment.

4.3.3 Conditions/Limitations

Conditions/limitations that were considered included tolerance for water, required processing time, and controllability of process conditions. Those treatments that could tolerate water up to about 40 percent would not require a drying step with its attendant fines control problems. Those requiring only 1 day for treatment could generally show a faster rate of cleanup than those requiring 3 days. Some biological processes required more than 3 weeks. The treatments generally provided control of the processing conditions; however, a few (e.g., composting) would not necessarily do so.

4.3.4 Concentration Range Handled

Concentration range handled in data developed for the processes ranged from unknown to 3,000 ppm. Some processes had limits inherent in the technology; others had no apparent limits.

4.3.5 Status of Development

Processes were found to range from concept stage to completed field tests. Most were in the pilot stage.

4.3.6 Test and Evaluation Data Needs

Data needs varied with the status of the process. At worst, data were available showing tests of the concept. At best, the process had been field tested, and only permits and checkout were needed.

4.3.7 Unit Operations

Unit operations employed in each process were identified. Collectively, the processes use 18 different unit operations. The number of operations per process varied from two to eight, depending upon the complexity of the technology.

4.3.8 Estimated Costs

Estimated costs (obtained as described in Section 4.4) were assembled graphically (see Figure 16 in Section 6).

4.4 COST ESTIMATES

4.4.1 Cost Estimation Methodology

Costs of applying an alternative technology are very difficult to predict because of the uncertainties regarding the potentially available new treatment processes. Estimates of the quantities of PCB-contaminated sediments are under review and may change significantly as a result of the reviews. In most cases, additional information is needed regarding the yet to be proven effectiveness of emerging treatment processes before the costs of their application can be assessed accurately. Therefore, the cost estimates presented here should be viewed as preliminary with respect to the new treatment processes. A range of costs is given for supporting operations (dredging and transportation) to reflect differences in different geographical areas of the country.

Because the regulations permit the use of incineration or chemical waste landfill and the application costs of these two methods are available from firms engaging in their practice, these costs were used as lower and upper limits with which to compare the costs of applying new alternative technology.

This provides a range of costs within which the alternative treatment processes could become attractive economically.

The application of any treatment process can involve the need for one or more of the following unit operations: dredging, transport, storage, landfill disposal, land treatment disposal, incineration, and/or alternative treatment. Estimates have been developed for all of these so that, in any given processing evaluation, the proper elements could be added to obtain an estimate of the cost of application. The estimates were made in terms of the cost per cubic meter of sediment treated. The sediment was assumed to have a density of 1.68 Mg/m^3.

The alternative treatment costs are based on current law; we assume that the treated sediments will be delisted.

Dredging costs for those treatments requiring removal of the sediment before treatment are estimated at $\$20/m^3$ based on the recent experience of the U.S. Army Corps of Engineers in contracting for dredging in the New York State area (Wheeler 1986).

Transport costs are given as a range. The Corps' experience is $\$13/m^3$ for short hauling distances. A cost of $\$126/m^3$ was used for long hauling distances, which represents an assumed 483-km average transport distance to RCRA landfills capable of accepting PCB-contaminated wastes (Industrial Economics, Inc., 1985).

Storage cost will sometimes be incurred to hold the dredged sediments pending treatment; e.g., where dredging rates exceed the rates at which the treatment can be applied. These have been set arbitrarily at $\$10/m^3$.

Land treatment involves the controlled application of wastes to the surface of the soil. At land-treatment facilities, wastes are either spread on or injected into the soil, followed by tilling into the soil with farm equipment. The physical and chemical properties of the soil, in unison with the biological component of the soil and sunlight work together to immobilize, degrade, and transform portions of the wastes. The application and tilling process can be repeated many times on the same plot, making land treatment a dynamic system designed to reduce and ultimately eliminate a portion of the waste, as opposed to permanent storage such as landfills.

The American Petroleum Institute (1983) has reported that there were 213 land-treatment facilities in operation handling waste from 16 different industry sectors. The most extensive use of land treatment is for petroleum refinery wastes, with 105 land-treatment facilities, many of which are located on the same site as the refinery. More recently, EPA verified the existence of 114 land-treatment facilities and obtained information on operating parameters at some of these sites (Thorneloe, 1986).

Wastes are typically mixed to a depth of 0.5 to 1.0 feet, where biochemical reactions take place. Application frequencies can range from daily to yearly, with tilling occurring as frequently as daily.

The average cost of controlled, managed land treatment cited by the American Petroleum Institute, \$60/ton, equates to \$111/m^3 of sediments. For short-term land treatment of readily-degradable solvents remaining in treated sediments free of PCBs after they are washed or dried, the cost is estimated at \$33/m^3 (Caplan, 1986).

Redeposition costs of decontaminated sediments were also estimated at \$33/m^3. Slightly lower costs might be expected in special cases.

Landfill disposal costs, incurred when the sediments must be placed in authorized chemical waste landfills, are estimated as ranging from \$260/m^3 for the Michigan area (EPA Regional Office) to \$490/m^3, based on the highest prices charged for hazardous wastes by commercial facilities (Industrial Economics, Inc., 1985). This range includes an intermediate value reported by the Corps of Engineers: \$420/m^3.*

---

*The New York State Department of Environmental Conservation has estimated that the costs of permitting and constructing a landfill facility for the Hudson River PCB Reclamation Demonstration Project would be approximately \$25/m^3 (M. P. Brown, 1986). The estimate includes site construction and cover costs, but does not include line items for land, overhead, profit, subsequent monitoring, and insurance costs. Since alternative treatment costs cited herein include overhead, profit, and insurance, they have been compared with the higher landfill costs cited above.

Costs for incineration techniques capable of achieving 99.9999 percent destruction and removal efficiencies for PCBs are difficult to predict. Even more difficult is prediction of the price commercial facilities will charge to accept the responsibility of handling such a sensitive waste. Surveys made to determine the likely charges to incinerate dioxin-containing wastes resulted in a reported price on the order of \$1,000/Mg (Pope-Reid Associates 1985). This translates to \$1,680/m^3, the value adopted for this evaluation, and the cost of disposal of residue from incineration is included. The total cost of use of incineration including dredging at \$20/m^3 and transport at \$13 to \$126/m^3 is \$1713 to \$1826/m^3.

When available, alternative treatment costs were obtained from the proponent of the process. Otherwise, they were estimated based on the types of unit processes involved and the environmental controls required, or they were determined not to be estimable considering the status of development of the process.

While all costs are in 1985 dollars, the treatment costs are not all necessarily based upon the same labor rates, corporate fixed charges, or profit. These costs vary from one firm to another. The cited estimates are costs of purchasing the treatments. Further cost analyses will be needed to provide a basis for comparison of processes on the basis of individual cost elements.

Table 2 shows the unit cost estimates used to develop cost ranges for the emerging treatments.

TABLE 2. UNIT COST ESTIMATES FOR STEPS INVOLVED IN TREATMENT AND DISPOSAL OF PCB-CONTAMINATED SEDIMENTS

Operation	Cost, \$/m^3
Dredging	20
Transport	13 to 126
Storage	10
Landfill disposal	260 to 490
Land treatment	33 to 111
Incineration	1,680

4.4.2 Baseline Cost Estimate

Baseline costs are taken as the range of costs for sediment removal, transport, and disposal in a chemical waste landfill. This range is calculated using the unit costs from Table 2:

Baseline costs, $\$/m^3$ = dredging cost and transport cost + disposal cost

= \$20 + \$13 to \$126 + \$260 to \$490

= \$293 to \$636.

4.4.3 Incineration Cost Estimate

Incineration costs include those for dredging, transport, and incineration. The cost of residue disposal is included in the incineration cost:

Incineration cost, $\$/m^3$ = dredging cost + transport cost + incineration cost

= \$20 + \$13 to \$126 + \$1,680

= \$1,713 to \$1,826.

4.4.4 Alternative Treatment Cost Estimate

The costs of alternative treatments are calculated in the same way, by summing the costs for the separate operations involved.

SECTION 5

ASSESSMENT OF ALTERNATIVE TREATMENT PROCESSES

The processes assessed in this section represent six different technologies; each of which is briefly described prior to discussing the processes to which it applies. For the process themselves, the depth of presentation varies because of the varying extent of available information.

5.1 PROCESSES BASED ON CHEMICAL TECHNOLOGIES

5.1.1 Supercritical Water Oxidation

5.1.1.1 Principles--

The supercritical water (SCW) oxidation process is a relatively low-temperature oxidation process that utilizes temperatures and pressures of supercritical water (above 374 °C and over 22.09 MPa) to break down hazardous organics to carbon dioxide, water, and other simple, less harmful molecules. The treatment is not selective but rather applicable to a broad range of compounds. Normally water-insoluble organics become highly soluble in supercritical water. The water also acts to reform complex organics, and heteroatoms, including halogens, phosphorous, sulfur, and metals, are readily precipitated as salts when present with appropriate counter-ions.

In the supercritical region, water exhibits properties far different from normal water. The density of supercritical water (0.05 to 0.3 g/mL) is low enough and the temperature high enough to essentially eliminate hydrogen bonding. As a result, the dielectric constant is reduced from 80 to less than 2, and water becomes a good solvent for organic substances (Thomason and Modell 1984). In contrast, inorganic salts become only sparingly soluble. Thus, the solubility characteristics of supercritical water are the inverse of those of normal liquid water.

In water above 350 °C, organic materials reform to low molecular weight products. Whereas many organic compounds tend to form a high molecular weight char at temperatures below 350 °C, in supercritical water the same organics are reformed to gases (e.g., CO, H_2, CH_4, CO_2) and volatile organic liquids (alcohols, aldehydes, furans) without producing char.

The products of supercritical water reforming can be subjected to oxidation while still under supercritical conditions. The residence time usually required for oxidation is less than 1 minute, which greatly reduces the volume of the oxidizer vessel. In addition, oxygen is completely miscible with supercritical water, and the oxidation can be conducted under homogeneous (i.e., single-phase) conditions. Contaminated sediments may not contain sufficient organics, and supplementary fuel would be required to maintain reaction temperatures.

When toxic or hazardous organic chemicals are subjected to SCW oxidation, carbon is converted to CO_2 and hydrogen to H_2O. The chlorine atoms from chlorinated organics are liberated as chloride ions. Similarly, nitrogen compounds will produce nitrogen gas, sulfur can be converted to sulfates, phosphorous to phosphates, etc.* Upon addition of appropriate cations (e.g., Na^+, Mg^{++}, CA^{++}), inorganic salts can be formed.

When the concentration of organics is above 5 percent by weight, the heat of oxidation is sufficient to bring the supercritical stream to temperatures in excess of 550 °C. At these conditions, inorganic salts have extremely low solubilities in water. Inorganic salts will be precipitated out and readily separated from the supercritical fluid. After removal of inorganics, the resulting fluid is a highly purified stream of water at high temperature (>500 °C) and high pressure (25.5 MPa). It can be used as a source of high-temperature process heat.

5.1.1.2 Modar SCW Process--

A schematic flow sheet for the MODAR process as applied to soil-slurry decontamination is presented in Figure 1. The process consists of the following steps:

1. PCB-contaminated sediments are fed as a slurry with 20 to 40 percent solids, as determined by some continuous flow bench-scale testing and

---

*Personal communication, William R. Killilea to Donald L. Wilson, April 11, 1986.

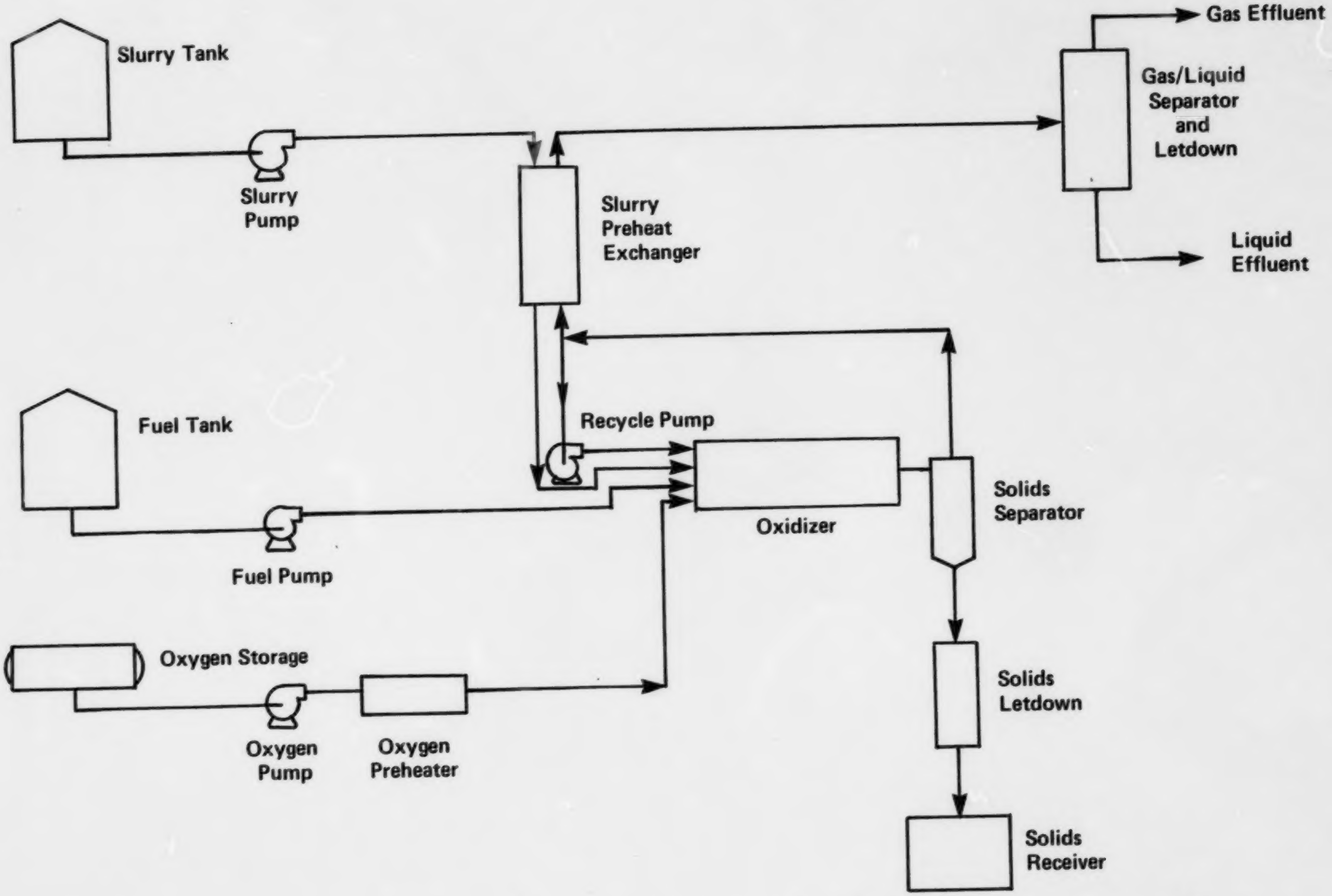

Slurry Tank
Slurry Pump
Slurry Preheat Exchanger
Gas Effluent
Gas/Liquid Separator and Letdown
Liquid Effluent
Fuel Tank
Recycle Pump
Fuel Pump
Oxidizer
Solids Separator
Oxygen Storage
Oxygen Pump
Oxygen Preheater
Solids Letdown
Solids Receiver

Figure 1. Schematic of the MODAR SCW oxidation process for sediment decontamination.

preliminary economic studies. The slurry is pressurized to supercritical pressure then heated by heat exchange with oxidizer effluent generated in a subsequent step.

2. At the oxidizer, pressurized oxygen, organic fuel, preheated slurry and oxidizer recycle are brought together. Because the water is supercritical, the oxidant is completely miscible with the solution (i.e., the mixture is a single, homogeneous phase). Organics are oxidized in a controlled but rapid reaction. Because the oxidizer operates adiabatically, the heat released by combustion of readily oxidized components is sufficient to raise the fluid phase to temperatures at which all organics are oxidized rapidly. For a feed of 5 percent organics by weight, the heat of combustion is sufficient to raise the oxidizer effluent to at least 550 °C.

3. The effluent from the oxidizer is fed to a salt and sediment separator, where inorganics and sediments originally present in the feed are removed as a solid slurry. At 500 °C and above, the solubility of inorganics in SCW is extremely low.

4. A portion of the superheated SCW is recycled to the SCW oxidizer by a high temperature, high pressure pump. This operation provides for sufficient heating of the feed to bring the oxidizer influent to supercritical conditions.

5. The remainder of the superheated SCW (with some CO_2) is used to preheat the incoming soil slurry.

As a waste destruction process, the Modar concept has several advantages. The chemical reactions that occur are carried out in a closed system, making it possible to maintain total physical control of waste materials from storage, through the oxidation process, to the eventual discharge of the products of combustion and any associated wastes.

In addition, bench-scale results indicate essentially complete destruction of chemically stable materials (such as PCBs) at projected costs that are well within those currently associated with hazardous waste operations. The process can be adapted to a wide range of feed mixtures and scales of operation. Skid-mounted, transportable systems are being designed as well as larger scale stationary units.

A liquid PCB waste treated by SCW oxidation at the CECOS International facility in Niagara Falls, New York, under permits, showed > 99.995 percent complete oxidation (Modar 1985). This percent oxidation would have been greater if the methods of analysis could have detected lower concentrations. The analytical detection limits for the effluent were < 0.1 ppb in the liquid and < 4.8 μg/SCM in the gas effluent. Process tests with feeds at higher concentrations, and lower effluent detection limits have shown 99.9999 percent oxidation (e.g. dioxin). The company plans to commercialize the process in 1986 for treatment of liquid PCB.

Bench-scale tests of dioxin-contaminated soils have shown reduction to background levels. The process is continuous, and the primary problems in its development for treatment of soils are the selection of pumps for slurries (20 to 40 percent solids) and the need for supplemental fuel sources to maintain heat input when trace concentrations are being treated.

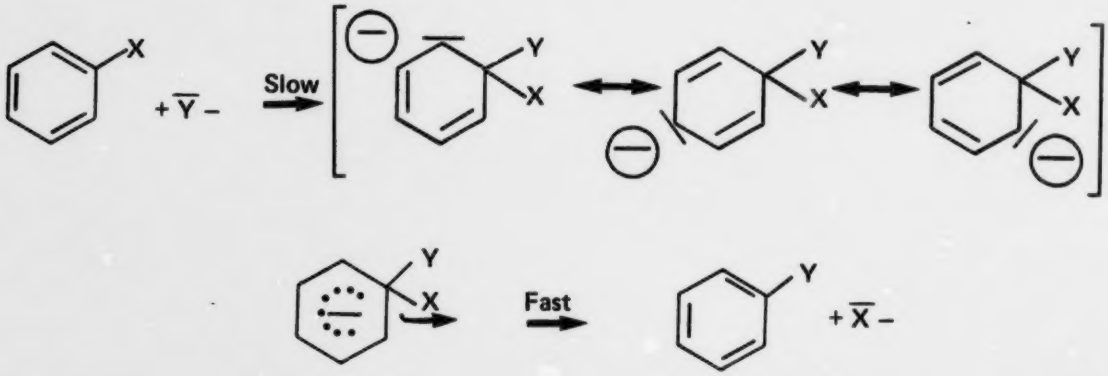
The Modar System has been tested for soils, and major problems in handling this type of process feed have been identified. The components would be constructed from corrosion-resistant, high-nickel alloys. Projected costs of treatment alone are \$184 to \$554/m^3 of PCB-contaminated sediment. Dredging would be required, as well as transport for treatment and redeposition of treated sediments. The overall cost estimate is thus:

$$\begin{aligned}\text{Cost, \$/m}^3 &= (\text{\$20 dredging}) + (\text{\$13 - \$126 transportation}) \\ &\quad + (\text{\$184 - \$554 treatment}) + (\text{\$33 deposition}) \\ &= \text{\$250 - \$733/m}^3.\end{aligned}$$

5.1.2 Nucleophilic Substitution

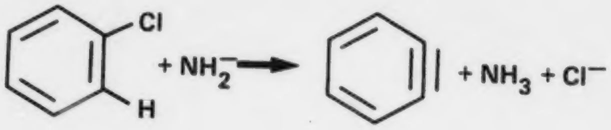
5.1.2.1 Principles--

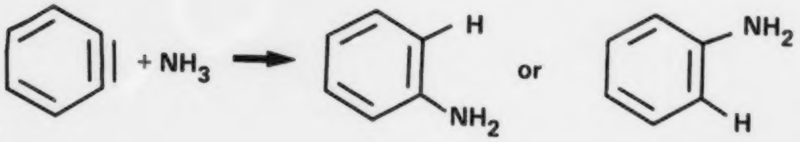
Nucleophilic (electron-donating) substitution removes chlorine from aromatic compounds by two mechanisms, the intermediate complex mechanism and the benzyne mechanism (March 1986). The intermediate complex mechanism consists of the following two steps, with the first usually rate-determining:



The resonance hybrid formed in the first reaction is represented by the structures within the brackets. These are shown in an alternative representation for reaction 2. The overall reaction rate is increased by the presence of activating groups (e.g., NO, NO_2) on the molecule.

The benzyne mechanisms occur on aryl halides such as PCBs, which require stronger bases than normally used because they lack activity groups on the molecule:





If the aryl halide contains two ortho substituents, this mechanism cannot occur.

Nucleophilic substitution using alkali metal hydroxides in poly (ethylene glycol) [PEG], or poly (ethylene glycol methyl ether) [PEGM] (Brunelli et al. 1985) has been shown to remove chlorine from PCBs. Chlorine removal probably involves alkoxide reaction, as illustrated by the following mechanism:

$$ArCl_n + ROK \rightarrow ArCl_{n-1} - OR + KCl$$

$$\text{Chlorinated aromatic} + \text{Potassium glycollate} \rightarrow \text{PEG ether}$$

The partially dechlorinated, water-soluble reaction product may continue to undergo dechlorination, depending on the reaction conditions.

The application of alkali-PEG (APEG) reagent to decontamination of PCB-contaminated soils and sediments is under investigation at EPA. The reaction proceeds rapidly at 70 to 100 °C. The degree of dechlorination can be controlled by modification of the reaction conditions. The KOH-PEG reagent tolerates a fair percentage of water. PCBs and other halogenated molecules are soluble in the reagent. Extraction of the PCBs from the soil is accomplished by adding a phase transfer agent to the reagent.

The number of nucleophiles that have been investigated for PCB dechlorination is small, relative to the number identified as affecting the substitution reaction. Although it is not possible to construct a nucleophilicity rank order that is invariant because different substrates and different conditions lead to different orders, an overall approximate order is: $NH_2^- > Ph_3C^- > PhNH^- > ArS^- > RO^- > R_2NH > ArO^- > OH^- > ArNH_2 > NH_3 > I^- > Br^-$ (March, 1968). Nucleophilicity is generally dependent on base strength, and it increases from atom to atom down a column of the periodic table.

Nucleophilic substitution by alkali reagents such as sodium naphthalide has been used extensively for dechlorination of PCBs in transformer oils. The reaction is fast, but it is not tolerant of water.

5.1.2.2 KPEG Terraclean-Cl Process--

5.1.2.2.1 Description--The KPEG treatment process is the subject of an in-house study at the Hazardous Waste Engineering Research Laboratory, of preliminary work on a conceptual treatment at New York University based on the high absorptive affinity of soils for PCBs, and of a process identified by Galson Research Corporation as Terraclean-Cl. Evaluation of this process is based upon data for the Terraclean-Cl version. A patent has been granted on this process and will be published in mid-1986.

The Terraclean-Cl process involves the chemical dehalogenation of PCBs under mild conditions. This is achieved by mixing the soil with an equal volume of hot (150 °C) reagent in a rotating mixer such as a converted cement mixer. Water coming in with the soil is volatilized and recovered for later use in the process. The reagent consists of a mixture of polyglycols and capped polyglycols (PEG and PEGM), potassium hydroxide (KOH), and dimethyl sulfoxide (DMSO). The exact formulation of the reagent is varied according to the specific soil and contaminant combination. The DMSO does not take part in the reaction but acts as a catalyst and phase transfer agent to extract the PCBs from the soil.

At the end of the reaction, usually 30 to 120 min, the bulk of the reagent (>80 percent in field tests) is decanted from the soil. A small part of the reagent remains on the soil, along with some of the dechlorinated reaction products. The residual reagent and dechlorinated by-products are removed from the soil by mixing the soil with an equal volume of water and decanting the water. This washing is done two or three times and provides >99 percent overall recovery of reagent. The washwater from the last wash is passed through a bed of activated carbon, which preferentially removes the dehalogenated products. The contaminated carbon is burned in a PCB incinerator. The overall process, including recycle streams, is shown in Figure 2.

The partially dechlorinated PCB continues to dechlorinate, with >98 percent of the chlorine associated with the PCB being recovered as KCl under some conditions. The DMSO does not take part in the reaction but acts as a catalyst and phase transfer agent, increasing both the rate of reaction and the rate of transport of PCB from the soil into the reagent.

Process kinetics for the Terraclean-CL process are affected by:

- Soil carbon content
- Soil particle size distribution
- PCB isomer distribution
- Water content of the soil
- Reaction temperature
- Reagent formulation.

High carbon soils give the slowest rates of reaction, with reaction times as long as 2 h for reduction to <1 ppm PCB. Very fine soils with poor percolation characteristics take longer to drain, although the constant mixing used during the washing steps reduces the time required for draining the soil. The rate of reaction for different PCB isomers is inversely proportional to their

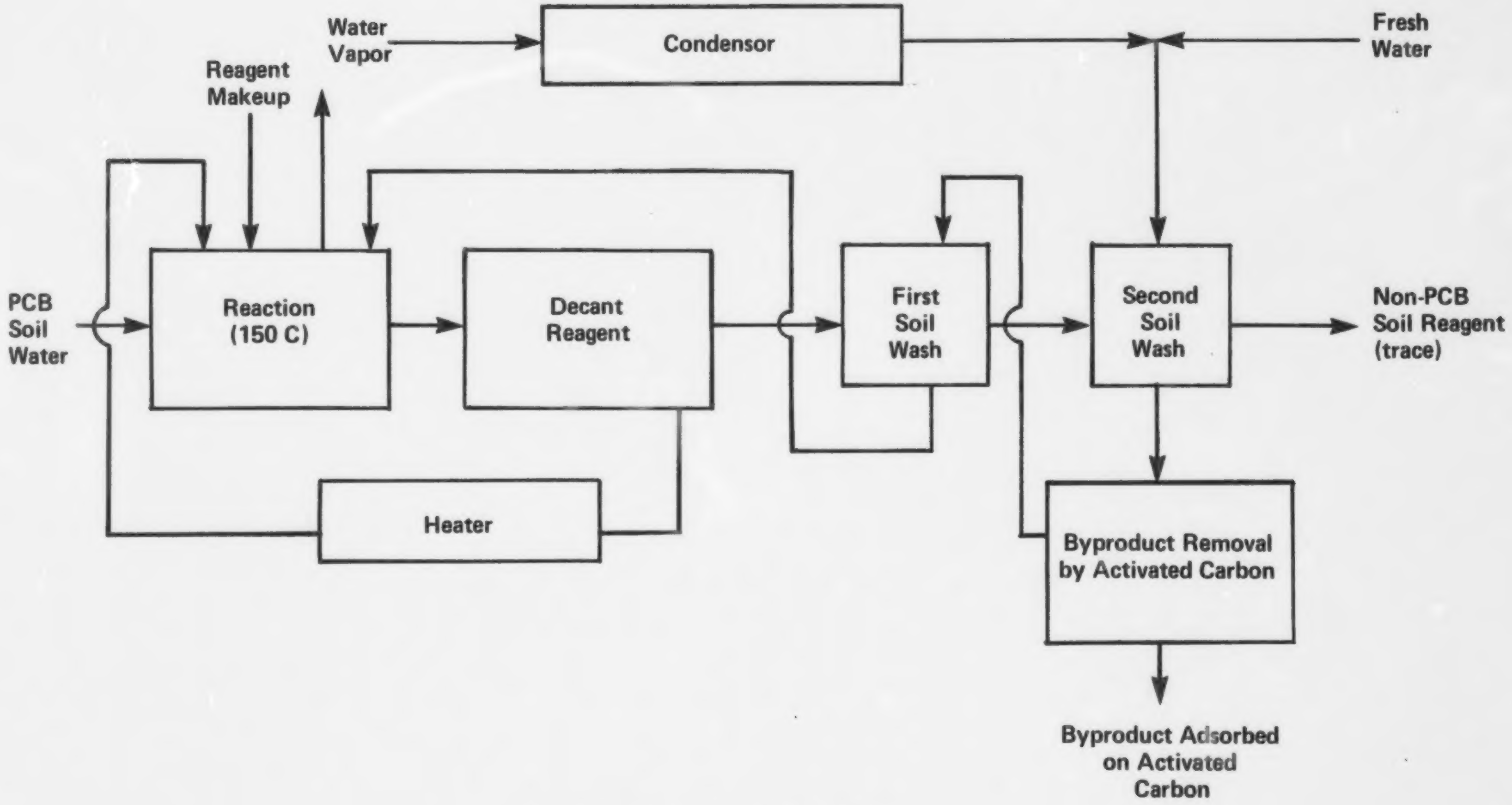

PCB
Soil
Water
Reagent
Makeup
Water
Vapor
Condensor
Fresh
Water
Reaction
(150 C)
Decant
Reagent
First
Soil
Wash
Second
Soil
Wash
Non-PCB
Soil Reagent
(trace)
Heater
Byproduct Removal
by Activated Carbon
Byproduct Adsorbed
on Activated
Carbon

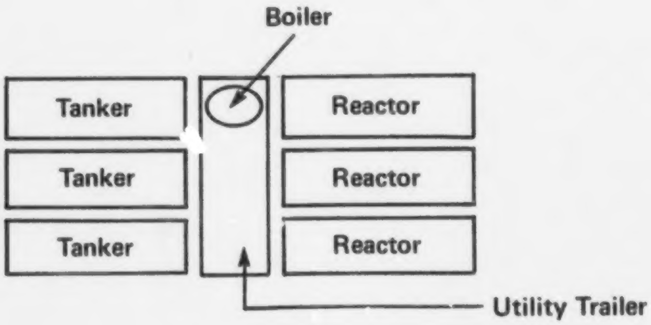
Figure 2. Schematic of kPEG process.

biodegradability, with the most heavily chlorinated isomers being the easiest to react. At reaction temperatures below 100 °C, the water content of the soil affects the rate of reaction. At reaction temperatures around 150 °C (the preferred reaction temperature), the initial soil water content is irrelevant because the water rapidly volatilizes. Dioxin-contaminated soils with initial water contents as high as 40 percent have been decontaminated rapidly using this process. The rate of reaction increases with temperature up to around 200 °C, where degradation and volatilization of reagents becomes a problem.

A variety of successful reagent formulations have been used in this process, each employing a different mixture of glycol/sulfoxide/hydroxide. Laboratory experience indicates that the optimum reagent formulation varies somewhat for different soils and patterns of contamination. At present, it is necessary to determine experimentally the optimum reagent formulation for each soil.

Under preferred reaction conditions, PCBs are reduced from 500 ppm to <0.1 ppm in 0.5 to 2.0 h. Residual PCB concentrations in treated soils can be <0.04 ppm as determined by solvent extraction/gas chromatography. The current laboratory and field test data support a fairly good mass balance (± 2 to 5 percent).

The Terraclean-CL process can be handled in several sizes of mobile (trailer-mounted) equipment. For use in cleaning Hudson River sediments, it is assumed that a total of 153,000 m^3 are to be treated over a 1-yr period. At a 75-percent utilization rate, this would require a nominal capacity of 570 m^3 per day. This could be supplied by a set of five treatment modules. Each module would consist of three reactor trailers, each with a capacity of 14 m^3, served by a single utility trailer and associated tank trailers:



Process flow rates for a single 14-m^3 capacity reactor trailer in this size system are shown in the flow sheet in Figure 3. Flow rates would be the same for each reactor trailer. This balance assumes incoming and outgoing soil at 40 percent moisture and 1 percent reagent loss. The actual values for these items will vary as a function of the soil characteristics.

The boiler sizing assumes a nominal reaction temperature of 150 °C. Temperatures in the range of 120 to 180 °C are acceptable. Much lower temperatures may extend the reaction time unnecessarily, and higher temperatures may cause reagent degradation or pressure buildup.

Because of the closed nature of the process, no pollution control equipment is likely to be required. The major potential problem is slow draining time caused by a buildup of fines on the reactor filter screens. This should be handled by the constant mixing of the reactor contents during the reaction and washing steps. The mixing should prevent buildup of an impervious layer during processing. This assumption is to be tested shortly using a pilot-plant unit to be built in mid-1986.

Laboratory-scale trials of this process have mostly processed soils contaminated with 1,2,3,4- or 2,3,7,8-tetrachloro-p-dibenzo dioxin. The small amount of PCB work in this area has been done as a preliminary to the dioxin studies. Dioxin levels in treated soil have been reduced to <0.06 ppb, although the usual detection limit has been in the area of 1.0 ppb. Of the four or five PCB soils tested to date, each has been reduced to <1 ppm PCB, although in some cases it has been necessary to vary the reagent formulation to achieve the desired result.

This process proceeded directly from laboratory- to pilot-stage testing, using modified 55-gal drums as the reaction vessels. As in the case with the laboratory testing, the pilot testing with PCBs was viewed primarily as a support activity for the dioxin testing. For that reason, the reagent formulation used was optimized for dioxin rather than for PCBs. Some of the results of the PCB testing include:

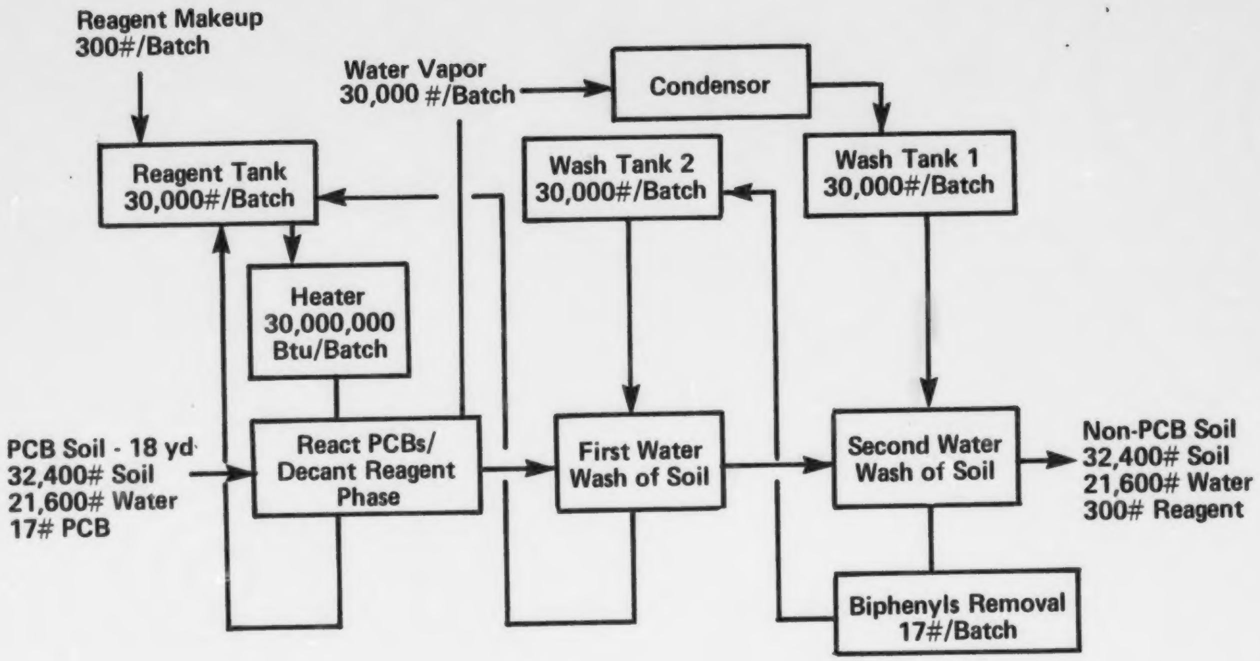

Reagent Makeup
300#/Batch
Water Vapor
30,000 #/Batch
Condensor
Reagent Tank
30,000#/Batch
Wash Tank 2
30,000#/Batch
Wash Tank 1
30,000#/Batch
Heater
30,000,000
Btu/Batch
PCB Soil - 18 yd
32,400# Soil
21,600# Water
17# PCB
React PCBs/
Decant Reagent
Phase
First Water
Wash of Soil
Second Water
Wash of Soil
Non-PCB Soil
32,400# Soil
21,600# Water
300# Reagent
Biphenyls Removal
17#/Batch

Figure 3. Schematic of scaled-up KPEG process.

Material	Weight of materials, lb Run 8	 Run 13
PCB soil	87	97
2-Methoxyethoxyethanol	39.25	44
Dimethyl sulfoxide	37.75	45
Potassium hydroxide	20	20
Water	40	20
Reaction temperature (°C)	100	100
Reaction time (h)	2	8
Initial average PCB concentration (ppm)	25.4	21.8
Final average PCB concentration (ppm)	0.9	0.8

This pair of runs demonstrated that temperatures as low as 100 °C were adequate to reduce PCB levels to <1 ppm and that reaction time was not a major factor in the overall degree of removal.

The apparatus used for decontamination of PCB-contaminated soils is shown in Figure 4. The apparatus consists of six items:

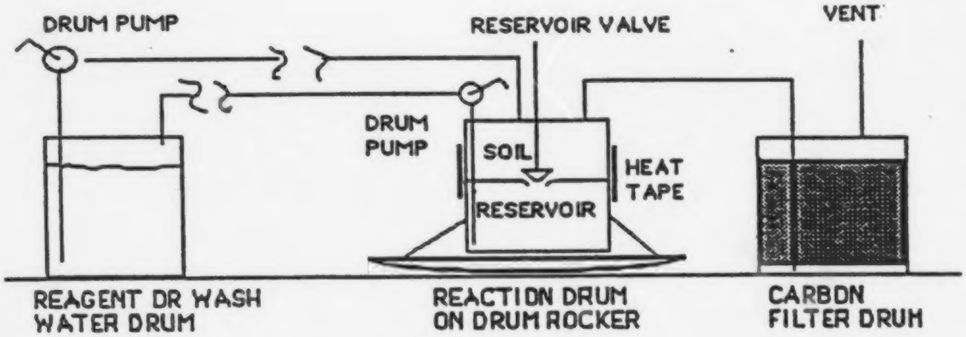

DRUM PUMP
RESERVOIR VALVE
VENT
DRUM PUMP
SOIL
HEAT TAPE
RESERVOIR
REAGENT OR WASH WATER DRUM
REACTION DRUM ON DRUM ROCKER
CARBON FILTER DRUM

Figure 4. Schematic of dioxin-treatment system.

- A two-section reaction drum with a section for soil on top of a reservoir for liquids. The two sections are separated by a steel plate with a valve in it. A drum pump is fitted into the lower section (liquid reservoir), and there are two taps into the top section. One tap allows liquids to be pumped into the drum, and the other tap is a vent. In addition, a thermometer well fitted with a bimetallic thermometer (not shown) is part of the top of the drum. A drum heater is wrapped around the drum, followed by Fiberglas insulation.
- A steel rocker, used to agitate the soil/reagent mixture by moving the drum and contents from side to side.

- A carbon filter drum attached to the vent from the reaction drum.
- Two drums used for washwater.
- One reagent recycle drum.
- A source of freshwater, either a drum or hose.

The test protocol used for testing the process consisted of the following tasks:

1. Obtain contaminated soil in 55-gal drums. Sample and analyze to determine initial PCB concentration.
2. Weigh approximately 45.4 kg (100 lb) of contaminated soil into a reaction drum, with the reaction drum resting on a scale. Wet the soil prior to transfer if dust generation is likely to be a problem. Sample drum contents and place lid on reaction drum.
3. Place heat tape and insulation around the reaction drum.
4. Attach the vent line to reaction drum and connect to carbon filter drum.
5. Place the reaction drum on the rocker.
6. Weigh reagents into the reaction drum from reagent drums using drum pumps on each reagent drum.
7. Turn on power to the heat tape and agitator and heat the reaction drum and contents to 150 °C, mixing during heating.
8. Allow reaction to proceed for the required time with mixing.
9. Turn off power to the heat tape and allow reaction drum contents to cool. Continue mixing during cooldown.
10. Open valve in reaction drum (see Figure 4) and allow reagent to drain into reaction drum reservoir. Continue mixing during cooldown.
11. Weigh reagent out of reaction drum reservoir into reagent recycle drum. Sample reagent.
12. Pump 45.4 kg (100 lb) water from water supply drum into the reaction drum and mix.
13. Allow water to drain into reservoir.
14. Pump water into wash drum 1. Sample water.
15. Pump 45.4 kg (100 lb) water from water supply drum into the reaction drum and mix.

16. Allow water to drain into reservoir and pump into wash drum 2. Sample water.

17. Open reaction drum, mix and sample soil. Seal drum for storage, pending analysis of soil.

5.1.2.2.2 Vent from reaction drum--The purpose of the vent on the reaction drum is to allow water vapor to escape. The carbon drum filter prevents the escape of any reagent or PCB vapors into the atmosphere, although analysis of vent streams in multiple laboratory samples did not show any cases where PCB vapors were vented under processing conditions.

5.1.2.2.3 Efficiency--The efficiency of the process for PCB removal from the soil varies with reaction temperature and reagent formulation. PCB removal to less than 1 ppm is routinely achieved, and PCB removal to <0.04 ppm has been demonstrated. Dioxin removal to the part per trillion (ppt) level has been demonstrated in the laboratory, and it is reasonable to assume that PCB reductions to that level are possible, although at present it would be extremely difficult to analyze soil samples at such a low level.

5.1.2.2.4 Reaction products--Analytical methods applied to the soil samples following reaction has been set up to identify any partially reacted PCB reaction products as PCBs. It is not known if there are any residual, totally dechlorinated PCBs in the soil, although it seems probable that these materials would be readily removed by the water wash. The water wash is passed through activated carbon to remove the biphenyl materials (see flow sheet) and the saturated carbon burned as a PCB waste. This practice has been devised as an alternative to proving the innocuous nature of the substituted biphenyls. Initial testing indicates that the substituted biphenyl products have an LD_{50} (oral-rate) >5 g/kg, indicating a very low degree of toxicity. Tests of the toxicity of the dioxin reaction products are under way at EPA, with initial tests indicating that the reaction products are not mutagenic (Ames test). Tests of chlorobenzene reaction products indicate that the reaction products do not bioaccumulate in fish.

5.1.2.2.5 Conditions/limitations--Conditions for successful processing of PCB soils to <1 ppm require reaction temperatures on the order of 100 to 150 °C and reaction times of 0.5 to 2 h. Total cycle times of 4 to 8 h are probable. Reagent is applied to the soil in a 1:1 ratio (dry basis) followed by reaction and reagent recovery. Reagent recoveries in excess of 99 percent have been obtained in PCB field testing. Initial soil water concentrations are not relevant to the process, except as it affects process economics because the water is volatilized during the heating step.

5.1.2.2.6 Energy usage- Energy requirements for the process are largely involved with heating moist sediments to 150 °C and removing the water by volatilization. For example, a sediment containing 40 percent water would require 4,818,000 kJ of energy per cubic meter, calculated as follows:

Mass of sediment		1680 kg
Mass of Water		
in sediment		1119.7 kg
in wash return		659.4 kg
Total		1779.1 kg
Mass of Reagents		1555 kg
Temperature rise		
volatilized water		100-20 = 80 °C
soil and reagents		150-20 = 130 °C
kJ required		
to heat water: 1779 x 4.18 x 80	=	594,898
to vaporize water: 1555 x 2,326	=	3,616,930
to heat sediment: 1680 x 0.84 x 130	=	183,456
to heat reagent: 1555 x 2.09 x 130	=	422,494
Total kJ		4,817,778

The cost of energy, assuming a cost of \$0.26/L #2 fuel oil and an energy value of 37,730 kJ/L, would be approximately \$33.20/m^3 of soil.

Full-scale (730 m^3/day) processing of Hudson River sediments could begin in 21 to 24 months. The events required include:

• Design full-scale (7-trailer) unit	6 months
• Construct first full-scale unit	6 months
• Test full-scale unit	3 months
• Construct additional units	6 months

5.1.2.2.7 Cost estimate--This process has not been scaled up to the size necessary for application to a site of this size. However, some initial cost estimates have been made and may be used as order of magnitude values.

Capital costs were estimated assuming a set of six treatment modules completely amortized over the life of the project. Costs for each module are comprised of the following items:

• Utility trailer	$600,000
• Reactor trailers (3)	$800,000
• Tank trailers (3)	$200,000
Total for each module	$1,600,000
Total for modules	$9,600,000
Capital cost, $/m^3	$25.11

This cost assumes an 8-h cycle time. If a 4-h cycle time can be achieved, the capital cost would be $4,800,000 or $12.56/m^3 of soil processed.

Other processing costs include reagents, energy, labor, and maintenance. These are estimated below:

- Reagent costs--At a usage rate of 1555 kg/m^3 of soil and an average cost of $1.65/kg/ a 1 percent loss equals $25.66 =

  1,423 x 0.01 x $1.65 = $25.66/m^3 soil

- Energy costs--At 40 percent incoming moisture = $33.20/m^3 (see previous calculation)
- Maintenance costs--Assume 10 percent of capital costs = $1.26 - $2.51/m^3
- Labor costs--Assume, for each module:

9 operators @ $300/day	$2,700
3 backhoe operators @ $350/day	$1,050
3 chemists at $400/day	$1,200
1 site manager @ $550/day	$550
Total	$5,500/24-h day

Processing rate = 124 to 247 m^3/24-h day (4- or 8-h cycle)

Manpower costs = $22 to $44/m^3.

This manpower cost estimate assumes that the sediments are moved from a storage area to the reactor. However, manpower costs would be reduced and the holding area eliminated if the sediments were moved by hydraulic dredge directly into the reactor, with the reactor serving to handle the gross dewatering of the sediments. Soil and water would be pumped to the reactor, which removes most of the water, retaining the bulk of the soil. Fine sediment particles are removed by a filter press, which is emptied periodically into a reactor. This approach would reduce the land area required and the labor involved, but it requires a closer fit between dredging capacity and reactor cycle time. Potential emissions of PCBs from holding areas would be eliminated, which may be a significant consideration:

Waste disposal - 2 kg activated carbon/m^3 soil at $1.10/kg = $2.20.

The total cost of application of the treatment process is estimated as follows:

Cost item	Cost, $/m^3	
	4-h cycle	8-h cycle
Capital	12.56	25.11
Reagent	25.66	25.66
Energy	33.20	33.20
Maintenance	1.26	2.51
Labor	22.00	44.00
Water disposal	2.20	2.20
Subtotal	96.88	132.68
Profit/contingency (50 percent)	48.44	66.34
Total	145.32	199.02

These costs do not include dredging or permitting costs. With dredging costs of $20/m^3, transportation costs of $13 to $126/m^3, and final placement costs of $33/m^3, total costs in the range of $211 to $378/m^3 are anticipated. Permitting costs are a separate item and would depend on the degree of cooperation given by the various regulatory bodies involved. However, the total costs are not highly sensitive to this item because permitting costs of $5,000,000 would only add $5/m^3 to the costs of processing.

5.1.3 Radiant Energy-Ultraviolet Light

5.1.3.1 Principles--

Ultraviolet (UV) radiation may drive chemical reactions in PCBs. The structure of the products of UV radiation alone are not well defined (Sworzen and Ackerman 1982). The primary reaction at wavelengths greater than 290 nm is stepwise dechlorination. Photolysis experiments in methanol at 298 to 313 K for 10 to 15 h showed that HCl was evolved. The products contained in the methanol solution consisted of dechlorinated PCB and certain methanol substitution products. The amount of methoxylated products did not exceed 5 percent of the total amount of products formed.

UV light energy, combined with a reducing environment, has been used to dechlorinate PCBs essentially completely in 1.5 to 2 h (Kitchens et al. 1982, 1984). Because the photochemical reaction is initiated by the absorption of light energy, the irradiation wavelength must match the absorption band associated with the chemical bond of interest in the molecule and the solvent must not absorb significantly at the irradiation wavelength. For PCBs, low-pressure mercury lamps that emit approximately 95 percent of their energy at 2,537 Å provide adequate irradiation.

Suitable solvents include water, alcohols, and hydrocarbons. However, these have very different effects on the process efficiency and mechanism. In heavy hydrocarbons, the dominant PCB reaction is the polymerization of the biphenyl radicals to yield polyphenylenes. In basic alcohol solutions, a stepwise dechlorination of the molecule occurs. This reaction occurs via the triplet state, and the reaction rate is dependent on the lifetime of that state. The hydrogen for the hydrodehalogenation initially comes from the solvent. In alcohol solutions, sparged hydrogen gas increases the reaction rate by removing triplet quenchers from the solution by combination with the solvent free radicals formed. In addition to the hydrogen, small amounts of sodium hydroxide are added to the alcoholic solution as a chlorine scavenger.

These photochemical reaction conditions lead to a rapid, highly controllable destruction of the PCBs, yielding only biphenyl and sodium chloride as the final products. Oxygenated derivatives, chlorinated dibenzofurans, or chlorinated dioxins have never been observed in the gas chromatographs or the mass spectra of the intermediates or products in the LARC degradation of PCBs.

5.1.3.2 LARC Process--

The LARC process (Light Activated Reduction of Chemicals, U.S. Patent 4,144,152) uses UV light and an optimized reducing environment to dehalogenate various chlorinated compounds extracted from soils.

Studies were performed to determine the extraction efficiency from soil of Aroclor 1260 using isopropanol as the extraction solvent (Kitchens et al. 1984). Isopropanol was chosen because it is a good LARC solvent, dissolves PCBs readily, and is relatively inexpensive.

For the initial extraction studies, a clay soil was used (2.0 percent organic matter; pH 5.6; Ca, Mg, P, and K levels were 660, 77, 56, and 20 mg/kg, respectively). Air-dried soil samples were spiked with Aroclor 1260 in acetone and thoroughly mixed; the acetone then was allowed to evaporate in a hood. Random subsamples of the soils were taken and Soxhlet extracted using a mixture of 50 percent acetone and 50 percent hexane. The extracts were diluted to the appropriate range and analyzed by gas chromatography.

Weighed amounts of dried, spiked soils were placed in four 1-L beakers (two for each chemical). Added to each of the four spiked soil samples were 100 mL of distilled water; these samples were thoroughly mixed to yield wet soils containing approximately 25 percent water. Then, 500 mL of isopropanol was added to each beaker and the mixtures stirred for 10 min. The liquid from each beaker was decanted and the volume measured. This procedure was repeated once. A portion of each extract was taken, diluted, and chromatographed as described above to determine the amount of halogenated organics removed from the soil in each extraction step. The soils then were air-dried, and a random sample was taken from each, Soxhlet extracted, and analyzed as above to determine the amount of Aroclor 1260 remaining in the soils.

One set of extractions of each chlorinated organic was combined and subjected to LARC using the single-lamp batch recirculation reactor shown in Figure 5. The reaction rates in this single-lamp reactor are significantly lower than in a multiple lamp, high-light-density reactor. However, only

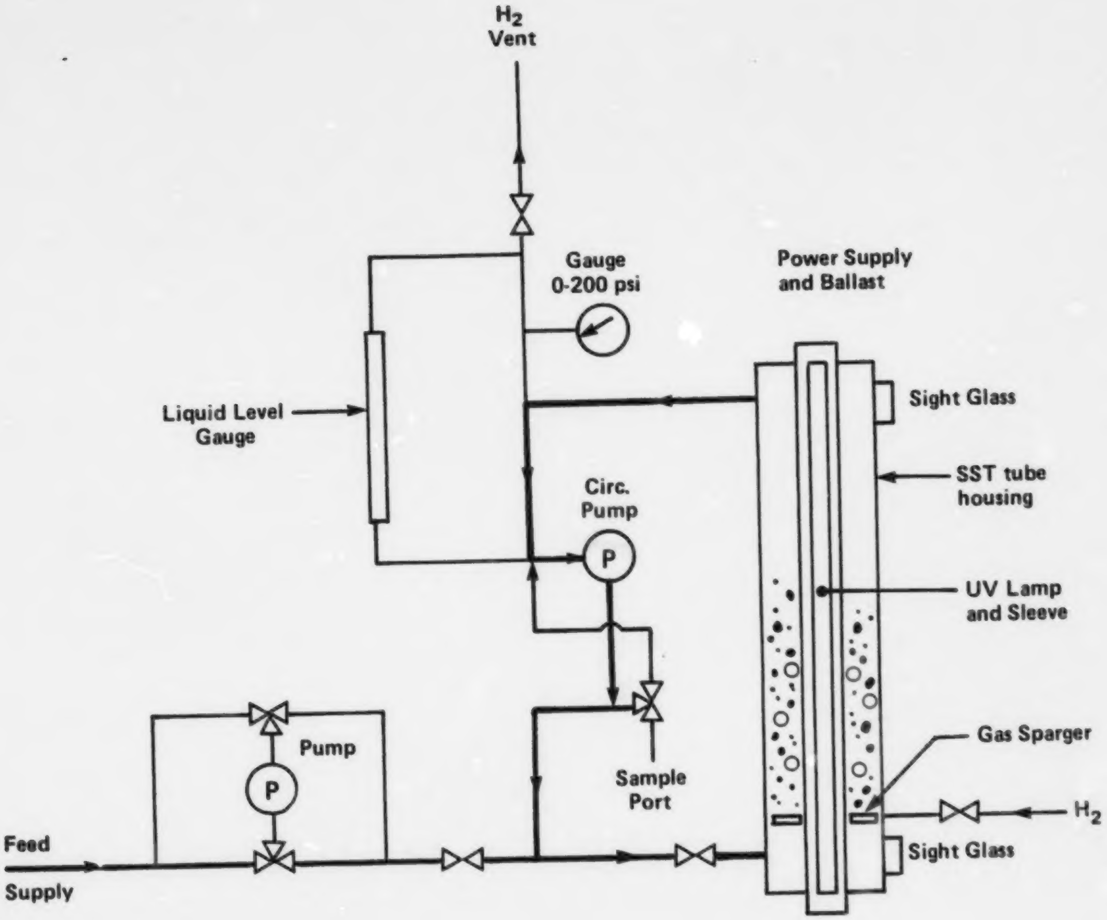

H_2
Vent
Gauge
0-200 psi
Power Supply
and Ballast
Sight Glass
Liquid Level
Gauge
SST tube
housing
Circ.
Pump
P
UV Lamp
and Sleeve
Gas Sparger
Pump
P
Sample
Port
H_2
Feed
Supply
Sight Glass

Figure 5. Schematic of single-lamp LARC reactor.

800 mL of solution is required for operation as compared to 30 gal for the 64-lamp pilot unit. Because the scaling factors between the two reactors were known, this single-lamp reactor was a convenient unit for evaluating the degradation rates under differing conditions.

Sodium hydroxide pellets were added to each set of extracts to form 2-percent solutions, and a portion of each solution was analyzed to determine the initial Aroclor 1260 concentration. The reaction was started by placing the solution into the reactor. The hydrogen gas then was turned on and allowed to purge the reaction mixture for 5 min. Then the UV light was turned on. Samples (10 mL) were drawn from the reactor after 20, 40, 60, 90, 120, and 180 minutes so that the degradation reaction could be followed and the reaction rate determined.

PCB analyses for the degradation were conducted using a Varian 3700 gas chromatograph and an autosampler with a Hewlett-Packard 5880 computer controller/integrator.

The results for the extraction of Aroclor 1260 from soil are summarized in Table 3. For dry soil, the Aroclor was extracted with an efficiency of 70 to 75 percent per stage and an overall two-stage efficiency of 92 percent. The single-stage extraction efficiency from wet soil was slightly lower than from dry soil (55 to 60 percent). Overall extraction efficiency based on the amount remaining in the soil was 90 percent. At least five stages of extraction would be required to achieve the goals of residual concentrations at background levels. The ratio of solvent to soil also may have to be increased from the 1.2/1.0 (wt/wt) used in these experiments.

The results of the LARC degradation of Aroclor 1260 in the isopropanol soil extracts are shown in Figure 6. Degradation proceeded rapidly, even in the presence of particulates with a pseudo first-order rate constant of 0.052/min. This was calculated based on the disappearance of all chlorinated species. In a larger reactor with a greater light density, the degradation rates can be expected to be 2 to 2.5 times those of the single-lamp reactor.

TABLE 3. EXTRACTION DATA FOR CHLORINATED ORGANICS FROM SOIL

	Aroclor 1260	
	Dry soil	Wet soil
Initial concentration (mg/kg)	487	486
Weight of soil (g)	330	330
Amount removed from soil in first extraction (mg/kg)	337	268
Solvent recovered from first extraction (mL)	320	360
Amount recovered from soil in second extraction (mL)	113	131
Solvent recovered from second extraction (mL)	420	410
Final concentration in extracted soil (mg/kg)	38	50
Overall extraction efficiency (%)	92	90

TABLE 3. EXTRACTION DATA FOR CHLORINATED ORGANICS FROM SOIL

	Aroclor 1260	
	Dry soil	Wet soil
Initial concentration (mg/kg)	487	486
Weight of soil (g)	330	330
Amount removed from soil in first extraction (mg/kg)	337	268
Solvent recovered from first extraction (mL)	320	360
Amount recovered from soil in second extraction (mL)	113	131
Solvent recovered from second extraction (mL)	420	410
Final concentration in extracted soil (mg/kg)	38	50
Overall extraction efficiency (%)	92	90

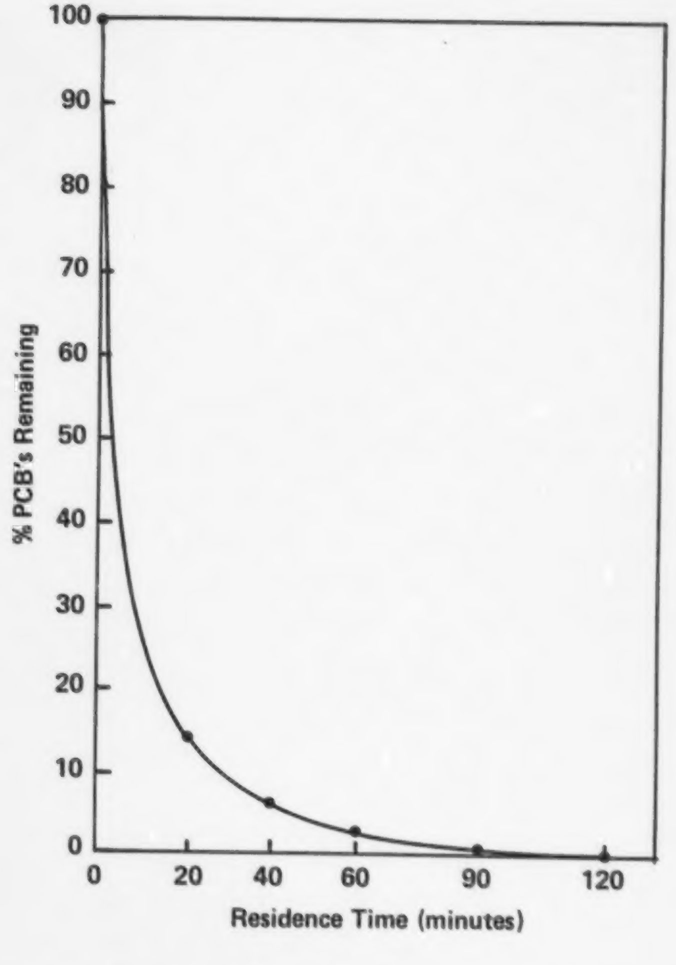


Figure 6. LARC degradation of Aroclor 1260 in basic isopropanol.

5.1.3.2.1 Efficiency--The laboratory tests indicate that PCBs can be extracted efficiently from both wet and dry soil using a solvent such as isopropanol (>99 percent). The PCBs in the extract can be successfully degraded by the LARC process. Any process must be capable of handling extremes in concentrations of PCBs and still maintain preset criteria for their removal from the soil and destruction.

5.1.3.2.2 Scale-up--The data from laboratory tests were used to design a mobile unit that can clean up spills of chlorinated organics from soils. A process schematic is shown in Figure 7. The equipment would be mounted in a standard trailer and consist of two extraction units to remove the chlorinated organics from the soil. After extraction, the soil would be vacuum-stripped to remove and recover residual solvent. The soil could then be returned to any suitable site. The extraction solvent would be sent to a still where the solvent would be recovered for reuse in the extractors and the chlorinated organics concentrated. Enough concentrate will be produced to provide feed for the LARC reactors on a continuous 24-h basis. Thus, the concentration entering the LARC units can be tightly controlled even though the concentration in the soil varied dramatically. This process design provides the flexibility to treat any type of soil at varying concentrations of chlorinated organics and still maintain optimum rates of reaction in the reactor. Costs for the removal of PCBs from soil and destruction by the LARC process are dependent on their average concentration in the soil. In most soils, high concentrations may be found close to the site of contamination. Once out of the immediate area, the concentration will drop off rapidly. However, if leaching has occurred, large areas contaminated at between 1 and 500 ppm can be expected.

5.1.3.2.3 Cost--The cost of treatment using this process has been estimated using an average concentration in the soil of 1,500 ppm (Kitchens et al. 1984). Cost items include daily operation, labor, analytical, travel, per diem, and profit. These total approximately \$157/m^3 of soil. Adding costs of dredging, transportation, and placement gives a cost range of \$223 to \$336/m^3.

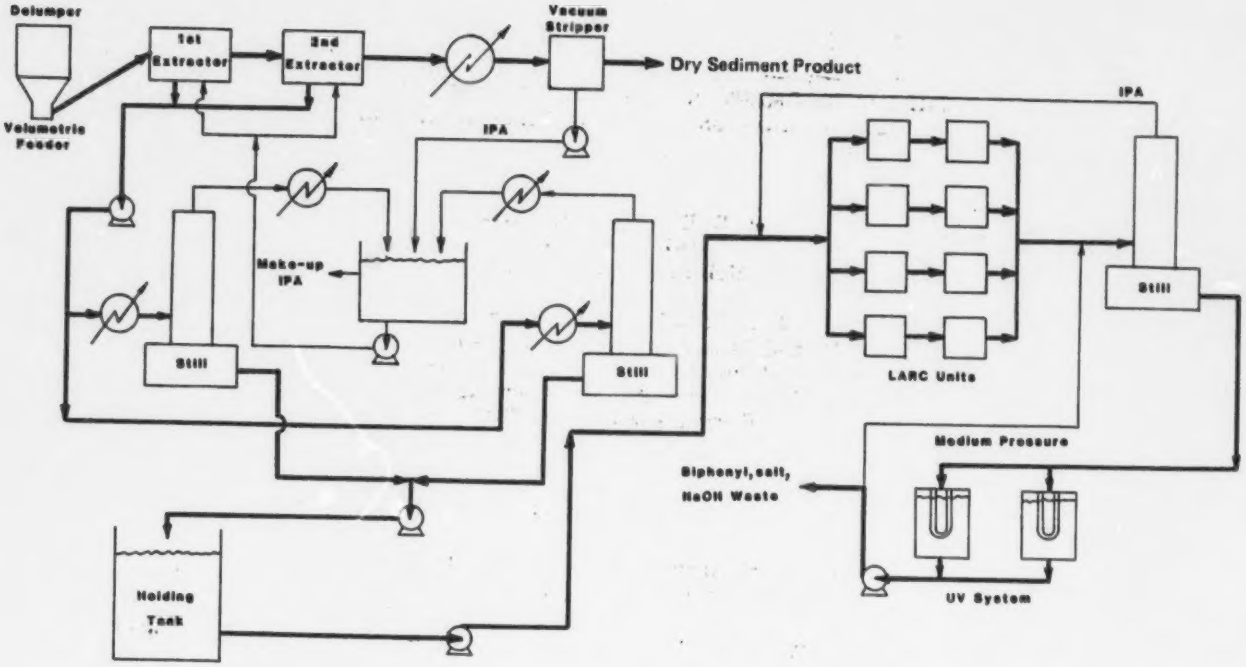

Delumper
Volumetric Feeder
1st Extractor
2nd Extractor
Vacuum Stripper
Dry Sediment Product
IPA
IPA
Make-up IPA
Still
Still
Still
LARC Units
Medium Pressure
Biphenyl, salt, NaOH Waste
UV System
Holding Tank

Figure 7. Schematic of LARC mobile unit for destruction of PCB's in soil.

5.1.4 Pyrolysis

5.1.4.1 Principle--

Pyrolysis is a thermal rupture of the chemical bonds of a molecule that destroys it without oxidation. The energy requirements vary with the material being processed. The use of pyrolysis requires the adoption of process designs that provide for transport of material that can melt, char, or become sticky during passage through a reactor. The design must provide for efficient heat transfer to the material so that it can be heated to 2,000 to 2,300 °C. Pollution controls are required to remove particulates and toxic components from exit gases. Feeds to pyrolysis units must usually be predried.

Compared to chemical processes, pyrolysis processes have higher energy requirements.

5.1.4.2 Advanced Electric Reactor, J. M. Huber Corporation--

The advanced electric reactor (AER) is a thermal treatment process. Pretreatment of the feed material is required. It must be dried to a moisture content of less than 3 percent and ground to 35 mesh particle size.

The process is patented, and all patents are owned by the J. M. Huber Corporation. The process is fully permitted under the Toxic Substance Control Act (TSCA) in EPA Region VI for the destruction of PCBs (permit received in May 1984).

As described in the trial burn report (J. M. Huber, October 31, 1983), the treatment process is based on a high-temperature fluid-wall reactor (Figure 8). The reactor heats organic compounds rapidly to temperatures in the range of 2,200 °C using intense thermal radiation in the near infrared. The reactants (in this case, nonliquid PCBs) are isolated from the reactor core walls by a gaseous blanket of nitrogen flowing radially inward through the porous core walls. Carbon electrodes are heated and, in turn, heat the reactor core to incandescence so that heat transfer is accomplished by radiative coupling from the core to the feed materials. The only feed streams to the reactor are the solid waste containing PCBs and the blanket gas (nitrogen). PCBs are destroyed by pyrolysis rather than oxidation. Therefore,

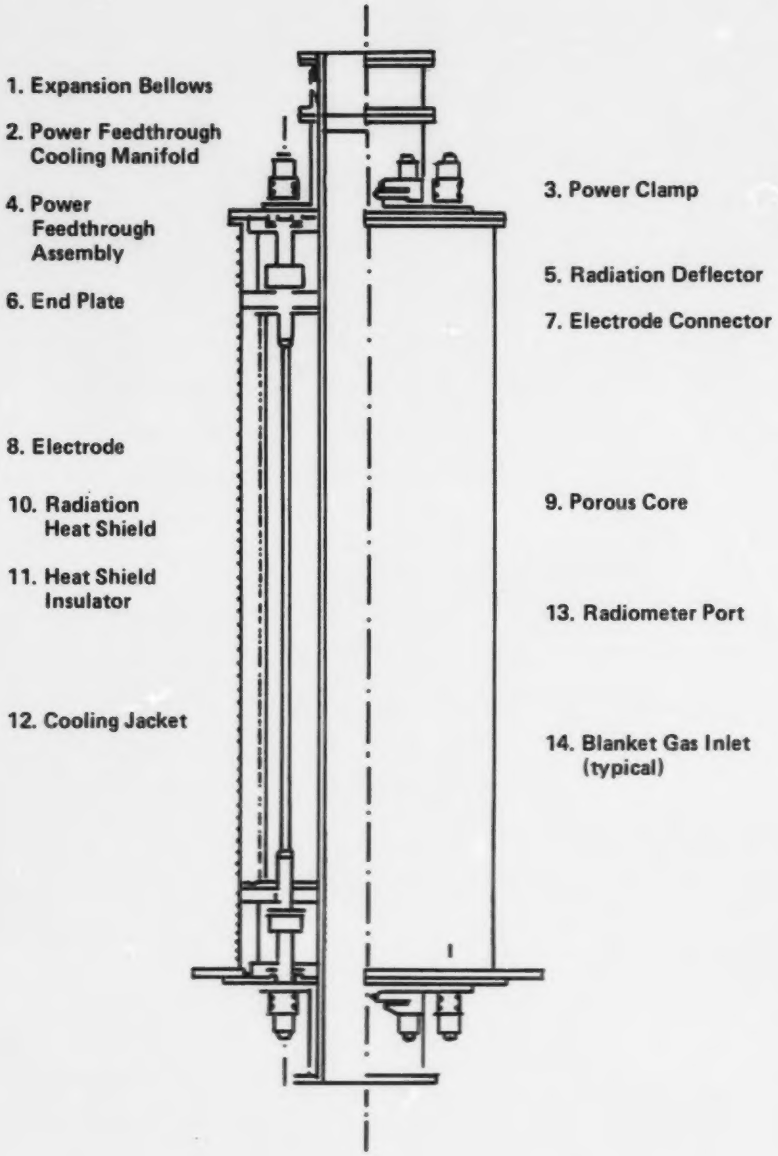

1. Expansion Bellows
2. Power Feedthrough Cooling Manifold
3. Power Clamp
4. Power Feedthrough Assembly
5. Radiation Deflector
6. End Plate
7. Electrode Connector
8. Electrode
9. Porous Core
10. Radiation Heat Shield
11. Heat Shield Insulator
13. Radiometer Port
12. Cooling Jacket
14. Blanket Gas Inlet (typical)

Figure 8. Vertical cross section of the Advanced Electric Reactor.

typical products produced by incineration such as carbon monoxide, carbon dioxide, and oxides of nitrogen are not formed in significant concentrations. The principal products of soil-borne PCB destruction are H_2, Cl_2, HCl, elemental carbon, and a granular free-flowing solid-derived waste.

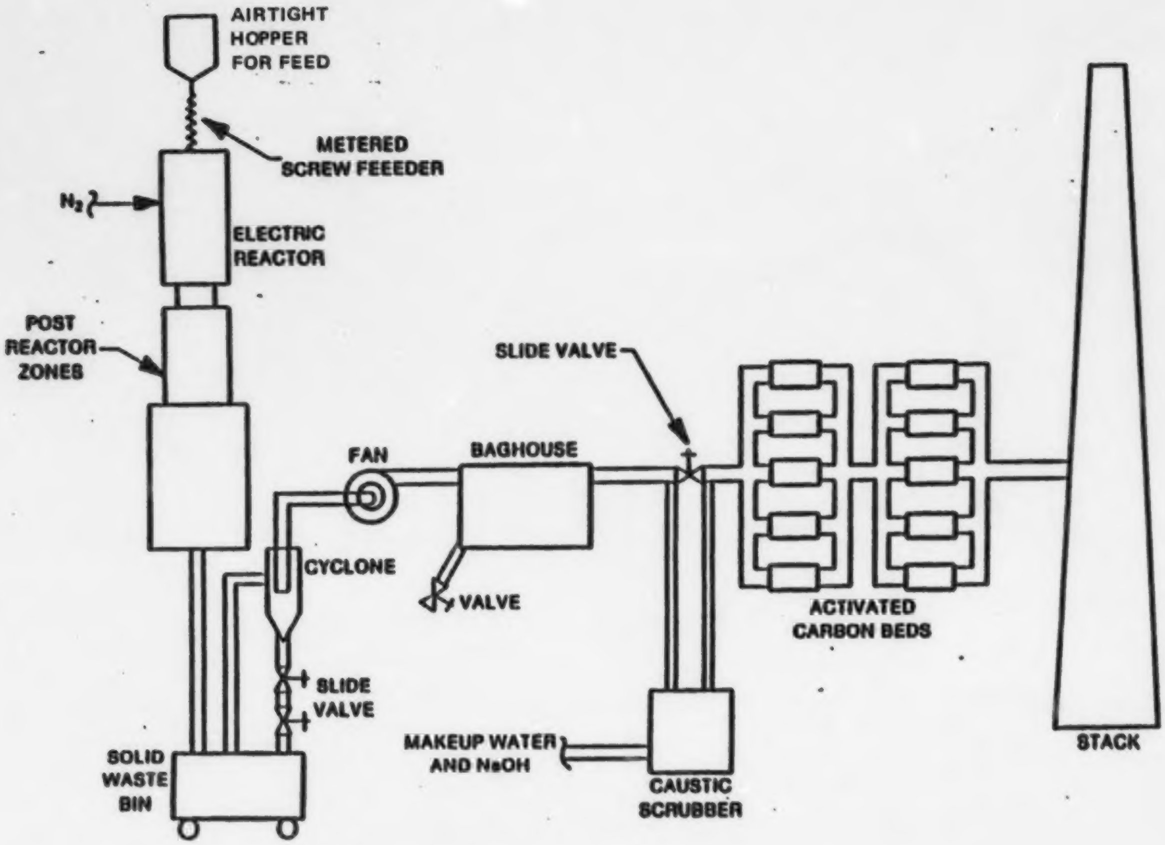
Figure 9 shows a simplified process diagram. The solid feed stream is introduced at the top of the reactor by a metered screw feeder connecting the air-tight feed hopper to the reactor. Nitrogen is introduced primarily at two points in the reactor annulus formed by the external containing vessel and the porous graphite core to create the fluid wall.

Small nitrogen streams are used to sweep sight glasses, prevent oxygen intrusion at the electrode ports, and similar nonprocess uses. Nitrogen flow is monitored by calibrated orifices in each feed line. The solid feed passes through the reactor where pyrolysis occurs. After leaving the reactor, the product gas and waste solids pass through two post-reactor treatment zones (PRTZ). The first PRTZ is an insulated vessel that provides additional high-temperature (~1,095 °C) residence time (~5 s), and the second PRTZ is water-cooled. It also provides additional residence time (~10 s), but it primarily cools the gas to less than 538 °C prior to downstream particulate cleanup.

The product gas then enters a baghouse for fine particle removal followed by an aqueous caustic scrubber for chlorine removal. Any residual organics and chlorine are removed by passing the product gas through two banks in series of five parallel activated carbon beds just upstream of the emissions stack. The organic-, particulate-, and chlorine-free product gas, composed almost entirely of nitrogen, is then emitted to the atmosphere through the process stack.

Solids exiting the PRTZ are collected in a solids bin that is sealed to the atmosphere. Additional solids in the product gas are removed by a cyclone and routed back to the solids bin. The solids collected in the solids bin are removed by plant personnel after each test or pair of tests.

5.1.4.2.1 Process operating parameters--The trial burn consisted of four tests conducted on 3 days. In all cases Aroclor 1260 was mixed with sand to


AIRTIGHT HOPPER FOR FEED
METERED SCREW FEEEDER
N_2
ELECTRIC REACTOR
POST REACTOR ZONES
FAN
BAGHOUSE
SLIDE VALVE
CYCLONE
VALVE
SLIDE VALVE
SOLID WASTE BIN
MAKEUP WATER AND NaOH
CAUSTIC SCRUBBER
ACTIVATED CARBON BEDS
STACK

(J. M. Huber).

Figure 9. Schematic of Advanced Electric Reactor process.

form a solid waste feed containing approximately 3,000 ppm PCBs. Carbon black was also mixed with the feedstock at approximately a 6.25:1 ratio to the PCB oil. This was equivalent to about 2.5 percent of the total feed mass. Carbon black functioned to enhance radiant energy transfer to the feedstock and to reduce coagulation of the sand particles.

There were no major differences in the process parameters for the four test periods. Feed rates were 7 kg/min to 7.2 kg/min with total feed masses ranging from approximately 1,580 kg to 1,927 kg depending on test duration. These feed rates were approximately halfway between the engineering design feed rates for the pilot plant of 4.5 kg/min and 9 kg/min. The nitrogen flow rate was held at 4 SCM/min for all test periods. Process temperature and scrubber pH also were essentially constant for the duration of the trial burn.

Process maintenance during the burn included changing the scrubber liquid after each test and emptying the baghouse filters.

5.1.4.2.2 Sampling methods--Sampling was performed using EPA reference methods when available, in some cases with appropriate modifications.

5.1.4.2.3 Removal by scrubber and carbon beds--Chloride removal in the product gas was accomplished by using a caustic scrubber installed prior to charcoal bed installation. Removal efficiencies based on scrubber inlet and stack concentrations indicate greater than 99.999 percent removal of chloride. This high efficiency may reflect chloride reacting with and/or being trapped by the carbon beds in addition to the expected 90 to 99 percent removal by the caustic scrubber.

5.1.4.2.4 Dechlorination of PCBs--Test data indicated that, in general, the chlorine content in the Aroclor 1260 was accounted for by Cl_2 and/or HCl at the scrubber inlet. Because there are no other sources for chlorine in the process except possible low levels of chlorine salts in the sand, it may be concluded that the chlorine content in the PCB feed is being converted to free chlorine in the reactor.

5.1.4.2.5 Test results and conclusions--The major thrust of the sampling and analytical effort carried out during the trial burn was the determination of PCB disposition in the process and PCB destruction and removal efficiencies. To accomplish these goals, PCB analyses (GC/MS) were performed for all effluent and waste streams, the PCB feedstock, and the process gas at the cyclone outlet. Other parameters that were measured included PCDDs and PCDFs in the cyclone outlet, major gas composition NO_x, chloride, particulate loading, volatile halogenated organic species in the stack and cyclone outlet, and chloride at the caustic scrubber inlet.

Results for the two potential solid waste streams, treated sand and baghouse filter catch, were in the range of 0.0005 µg/g to 0.001 µg/g (0.5 ppb to 1 ppb) and 0.024 µg/g to 0.53 µg/g (24 ppb to 530 ppb) PCB, respectively. These values are all well below the 50 µg/g (50 ppm) lower limit set for solids to be treated as hazardous wastes (40 CFR 761.60 Subpart D). These data indicate that for PCBs both streams can be considered nonhazardous wastes for disposal. The PCB concentration determined for the posttest charcoal was 0.001 µg/g (1 ppb) and was lower than that of the pretest sample. Both values closely approach detection limits. These data indicate that for PCBs the activated charcoal can be considered nonhazardous for disposal. However, surrogate recoveries may be artificially high due to spiking of the extraction thimble rather than the charcoal. Therefore, these data are not conclusive because the actual recovery of PCBs from the charcoal may be lower than indicated.

The only liquid waste produced by the AER process was the scrubber liquid. Although the results of the PCB analyses were variable, ranging from 0.29 µg/L to 2.7 µg/L (0.29 ppb to 2.7 ppb), all determined concentrations were well below the 50-mg/L (50-ppm) lower limit set for liquids to be treated as hazardous wastes (40 CFR 761.60 Subpart D). These data indicate that for PCBs the scrubber liquid can be considered nonhazardous.

Gas samples were taken at the cyclone outlet and stack using modifications of EPA Method 5. PCB concentrations ranged from 4.1 µg/SCM to 21 µg/SCM for the cyclone outlet. Stack concentrations were approximately one to two orders of magnitude lower, ranging from 0.03 µg/SCM to 0.30 µg/SCM. The high stack blank value reflects interferences due to overheating during sample preparation and represents the interferences in ions 292 and 326. Blank subtraction was not performed for determining destruction and removal efficiencies.

5.1.4.2.6 PCB destruction and removal efficiencies--Destruction efficiencies (DE) for the AER reactor were determined by comparing PCB concentrations at the cyclone outlet to calculated gas phase feed concentrations based on solid feed concentrations and feed rates. Destruction and removal efficiencies (DRE) were determined by comparing PCB concentrations at the stack to calculated gas-phase feed concentrations.

Two sets of DE's were computed: one based on weighed feed concentrations (3,000 ppm in the solid feedstock) and the other on analyzed feed concentrations. For both bases, the minimum DE was 99.9995 percent, with results ranging from 99.9996 to 99.99995 percent based on weighed feed concentrations (process data) and 99.9995 to 99.99995 percent based on analyzed feed concentrations. Two sets of DRE's were also calculated: one based on weighed feed concentrations and the other on analyzed feed concentrations. In all cases, regardless of calculation method, the DRE's exceeded 99.99999 percent. Efficiencies were at least an order of magnitude greater than the criterion established for incinerators by TSCA (40 CFR 761.760 Subpart D).

5.1.4.2.7 Conditions required for successful processing--The AER requires approximately 1,100 kWh per ton of soil treated. Operation of the required pretreatment equipment (crushers, grinders, etc.) and other auxiliary items use an additional 200 kWh per ton of soil.

The soil must be dry and sized to 35 mesh or smaller before it is fed to the reactor. Moisture concentrations of 3 percent can typically be accommodated. However, this may vary depending on the characteristics of the soil.

5.1.4.2.8 Cost--For very large volume cleanups, a cost estimate of \$412/ton (\$763/m^3) was supplied by J. M. Huber, strictly as a budgetary cost figure and not as an absolute or a quotation. This amount does not include the costs of dredging, transporting soil to the AER site, or facilities for storage of dredged soil. It also does not provide for cost of landfilling or other disposal of the treated sediment.

The capital cost for construction and initial testing of a single 25,000-ton/year transportable AER is approximately \$4 million, not including permits and trial burns. With six units, it would require approximately 3.5 years to treat 382,000 m^3 of sediment.

Dredging would be required, also transport for treatment and redeposition of treated sediments. The overall cost estimate is thus:

$$\begin{aligned}\text{Cost, } \$/m^3 &= (\$20 \text{ dredging}) + (\$13 - \$126 \text{ transportation}) \\ &\quad + (\$763 \text{ treatment}) + (\$33 \text{ deposition}) \\ &= \$829 - \$942/m^3.\end{aligned}$$

5.1.5 Thionation

Thionation introduces sulfur into an organic molecule to displace chlorine. The possible use of sulfur reactions to degrade pollutants has not been systematically exploited. Macallum (1984) showed that, at 150-170 °C, sulfur and sodium carbonate react with p-dichlorobenzene, removing the chlorine to form an insoluble polymer, sodium chloride, and carbon dioxide. Von Meyer (1986) conducted limited tests of a mixture of dried loam soil sparged with mixed dichlorobenzenes (DCBs), sodium carbonate, and sulfur. The dichlorobenzenes were added as a 0.01 g/ml solution in acetone. Reaction was carried out in a tilted 500-ml flask fitted with a condenser and sodium carbonate trap. The trap was required to remove hydrogen sulfide gas evolved during the reaction. The reactants were mixed periodically by rotating the flask a quarter turn every two hours over the 9 hour reaction period. The temperature ranged to 88 °C, and rose in the eighth hour to 260 °C when an exothermic excursion followed evaluation of volatiles formed from the sulfur. The results, based on analyses by thin layer chromatography and gas chromatography, were as follows:

1,2 dichlorobenzene:	8.4 percent dechlorinated 3.4 percent volatilized
1,3 dichlorobenzene:	90.8 percent dechlorinated 3.4 percent volatilized
1,4 dichlorobenzene:	91 percent dechlorinated 1.4 percent volatilized.

This is the extent of Von Meyer's investigation of the application of thionation to contaminated soils. As part of his study, DCB's and three chlorinated pesticides (Dieldrin, Lindane, and Heptachlor) were treated directly with two reagents: sodium polysulfide in an ethylene glycol-water media, and sulfur in ethylene glycol. With water present, the organics were all consistently volatilized at the 108-114 °C reaction temperature. The sulfur-ethylene glycol reagent degraded Dieldrin 99 percent and Lindane 90 percent. Heptachlor was not tested with this reagent.

Thionation is in the early stages of investigation, and a process for treatment of PCBs has not been sufficiently identified to permit further evaluation.

5.2 PROCESSES BASED ON PHYSICAL TECHNOLOGIES

5.2.1 Extraction

5.2.1.1 Principles--

The term "extraction" is employed to cover not only liquid-liquid extraction but also leaching of solids with organic solvents. Extraction of PCBs from a contaminated soil or sediment is emerging as a prerequisite for most chemical processes. PCBs are first extracted using a suitable solvent, and the obtained PCB solution is then subjected to one of the processes for destruction of the PCBs. Proven solvents include kerosene, methanol, ethanol, isopropanol, furfural, dimethyl formamide (DMF), dimethyl sulfoxide, ethylene diamine, and Freon mixtures. Supercritical fluids such as carbon dioxide have also been considered. Destruction of the dissolved PCBs is accomplished by a chemical reagent such as APEG detoxification, or the PCBs are concentrated by distillation or adsorption on carbon to give an RCRA waste that can be incinerated.

Water with and without 1 percent Tween 80 surfactant was shown to remove PCBs by less than 50 percent. The additive increased removal from inorganic soils but appeared to inhibit removal from organic soils (Scholz and Milanowski 1984). The results in Table 4 show substantial residual amounts of PCBs.

TABLE 4. EXTRACTION OF PCBs FROM
SOILS, EFFECT OF TWEEN

Soil	Solvent	Soil Dose (ppm PCB)	Percent removal	Residual (ppm PCB)	Supernatant Concentration (mg/L)
Inorganic	Water	3,000	24.6	2,660	72
	1% Tween 80	3,000	37.5	1,880	110
Organic	Water	26,000	48.3	13,200	418
	1% Tween 80	26,000	23.8	19,500	366

Hancher et al. ("Soilex" process, 1984) reported pilot plant data showing an estimated 85 percent removal of PCBs from soils using a kerosene-water mixture. The kerosene solubilized the PCBs and attendant other oils, and the water helped break up the soil particles. The mixture ratio found to give the most complete extraction of PCB was one part of soil to three parts of kerosene and three parts of water.

Adams et al. (1985) showed that the rate of liquid-liquid extraction of PCBs from oils solution by APEG reagents could be substantially increased by adding dimethyl sulfoxide (DMSO) or ethylene diamine to the hydroxide/PEG phase. The reagent with DMSO reached <2 ppm PCB after 30 min versus about 400 min for the reagent without DMSO.

Weitzman (1985) reported that repeated washings of PCB-contaminated soils with Freon-type solvents reduced the residual loading to <2 ppm. The soil types tested were sand-clay mixtures and a dark loam. PCB loadings to 1,983 ppm were leached in an agitated extractor.

Chu and Vick (1985) reported that the use of isopropanol as a cosolvent with DMF enhanced the reduction of PCBs by zinc in the presence of nickel catalyst.

O. H. Materials (Caron, 1985) is using methanol to extract PCBs from predried contaminated soils in a Superfund cleanup project at Minden, West Virginia. The soil is reduced to <25 ppm PCB and land-farmed. Further reduction in PCB concentration could be achieved using more stages of extraction. The PCBs in the extract are concentrated by adsorption on carbon, and the spent carbon is incinerated as an RCRA waste.

5.2.1.2 Acurex Solvent Wash Process--

The Acurex process is based on solid/liquid extraction (Weitzman 1984, 1985). A proprietary solvent is used, having been selected by comparisons of adsorption isotherms and PCB diffusion rates into several fluids: pure hexane, pure FC-113 (1,1,2-trichlorotrifluoroethane), a proprietary solvent blend, and an FC-113/hexane blend. With the pure Freon and topsoil, the equilibrium was favorable; however, it took up to 18 h for the system to reach equilibrium. Other solvents and solvent combinations were found that reduced the time to reach equilibrium to 30 to 40 min, a practical value.

Based on these fundamental studies, calculations showed that the ratio of PCB concentrations y_n and y_{n-1} in the liquid leaving the nth and (n-1)th washes, respectively (fresh liquid into each stage), was constant at 0.5:

$$0.5 = y_n/y_{n-1} .$$

This value proved to be reasonably independent of the type of soil being cleaned and the PCB concentration in the soil itself. The wash liquid leaving a wash would thus have a PCB concentration of approximately half that of the preceding wash.

The process was pilot tested using the proprietary solvent to extract the PCB from the soil. The PCB was then concentrated and the solvent reclaimed. Final PCB concentrations of less than 2 ppm on the soil were achieved.

The system was designed and built in late 1984. It was operated using non-PCB soils and shown to perform to design specifications. A permit to operate the system with PCB-contaminated soil was obtained in February 1985. Eight sets of tests were conducted, and these demonstrated that soils containing up to 1,983 ppm PCB were successfully treated to less than 2 ppm. In addition to demonstrating this pilot- scale system, these tests provided design data for construction of a full-scale proto-type soil-washing system. The results of these tests are summarized in Table 5.

TABLE 5. RESULTS OF SOIL-CLEANING TESTS, ACUREX SOLVENT WASHING PROCESS

Run number	PCB (ppm) By amount of PCB added	By analysis	By amount of PCB removed	Number of washes	Final PCB concentration (ppm)
1	37	38	38	3	<2
2	503	492	436	10	<2
3	---	67	72	6	<2
4	---	135	141	6	<2
5	---	548	1,941	12	<2
6	---	832	910	12	<2
7	---	773	678	10	<2
8	---	18	16	5	<2

Source: Weitzman 1985.

Figure 10 gives the schematic of the pilot soil-washing system. It consists of a soil contactor, dirty and clean solvent storage tanks, a solvent reclamation system, steam generator, and ancillary piping equipment. It also includes vent condensers and an activated carbon adsorption system for air pollution control. Operation proved very simple; one person had no difficulty operating it. Based on the results obtained with this system, a 5.4-m^3 mobile soil-washing system was designed and is now under construction.

The soil contactor is a semicylinder 1.2 m in length with a radius of 0.6 m. The soil washer is subdivided into two wash chambers along its axis. The volume of each wash chamber is 0.3 m^3. The isolated chambers allow operation of the soil washer with two different batches of soil at a time. Access to each chamber for soil loading and removal, or to obtain soil samples for analyses, is through two hinged lids that comprise the entire flat side of the semicylinder. The lids are sealed with a Neoprene gasket and are clamped to the main body for operation.

Each wash chamber is subdivided by filters installed in presses isolated in slotted holders at each end of the central soil chamber. The available volume in the soil chambers is 2 m^3, although the chambers were not filled entirely during operation. Approximately 0.2 metric ton of soil was cleaned during each test.

The washer is mounted to a frame by the shaft along its axis. It is rocked about its axis to agitate the soil/solvent mixture. It has a drive mechanism for rocking the washer that swings the contactor 90 degrees in either direction. Based on these successful results, field tests are planned for a site in St. Louis, Missouri. The process tolerates up to 40 percent water in the PCB extraction step.

5.2.1.2.1 Costs--Basic estimated costs for the treatment alone range from \$130 to \$390/m^3 (Weitzman 1985). Adding costs for dredging, transport, and placement of the treated sediments gives a total cost estimate of \$196 to \$569/m^3.

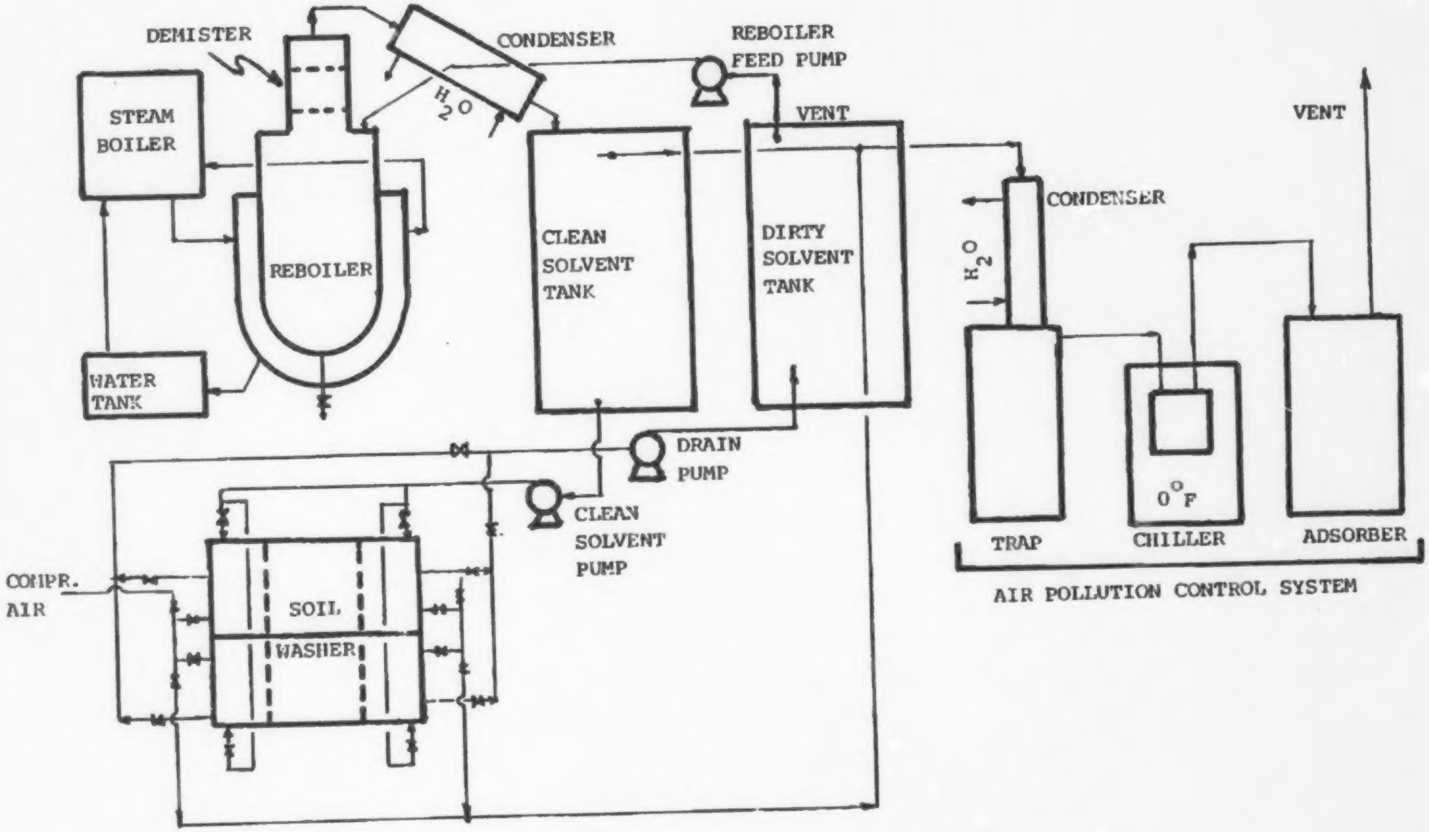

DEMISTER
CONDENSER
REBOILER
FEED PUMP
STEAM
BOILER
H_2O
VENT
VENT
REBOILER
CLEAN
SOLVENT
TANK
DIRTY
SOLVENT
TANK
CONDENSER
H_2O
WATER
TANK
DRAIN
PUMP
CLEAN
SOLVENT
PUMP
0^oF
COMPR.
AIR
SOIL
WASHER
TRAP
CHILLER
ADSORBER
AIR POLLUTION CONTROL SYSTEM

Figure 10. Schematic of Acurex solvent wash process.

5.2.1.3 O.H. Materials Methanol Extraction Process*--

The O.H. Materials methanol extraction process is being field tested in an EPA Region III sponsored cleanup of PCB-contaminated soil at Minden, West Virginia (Robert Caron 1986). The process involves slurrying the ground and predried soil with methanol, separating and redrying the treated soil, and solvent cleanup for resale. The cleanup employs activated carbon, which is subjected to incineration (other treatments could be used) as an RCRA waste. The cleaned soil is subjected to light land farming for degradation of any residual methanol. Wastewaters are treated in a holding pond.

The field test report for this process is to be issued during the next 6 months. The description and evaluation given here are based upon the findings to date, as obtained from the EPA Regional Office and from O.H. Materials.

A conceptual flow sheet for the process, Figure 11, was prepared to represent the system for evaluation purposes. The system size, 9.1 Mg/h (10 ton/h) corresponds with the size of unit used in the field test. The process consists of the following steps.

1. The toxic sediment is crushed to a size range suitable for drying. A Grizzly grinder was used and performed satisfactorily for the material processed (soil containing 15 percent water).

2. The sediment is dried to a water content of 5 percent. Drying is carried out under negative pressure. Hollow Flite dryers were used. In larger cleanup operations hot-oil-heated dryers of the same type would provide greater capacity using commercially available dryers of the same type.

   The air flow rate was about 42 m^3/min (1,500 ft^3/min). Pollution controls were used for cleanup of the exit gases and the particulates recovered from the scrubbers were subjected to the methanol extraction along with the dried sediments.

3. The dried sediment, plus recovered fines, was subjected to countercurrent extraction. The field test achieved a reduction from 400 to

---

*The O.H. Materials Corporation has subsequently merged with the Envionmental Testing and Certification Corporation to form the Environmental Treatment and Technologies Corporation.

PCB Decontamination Process, O.H. Materials

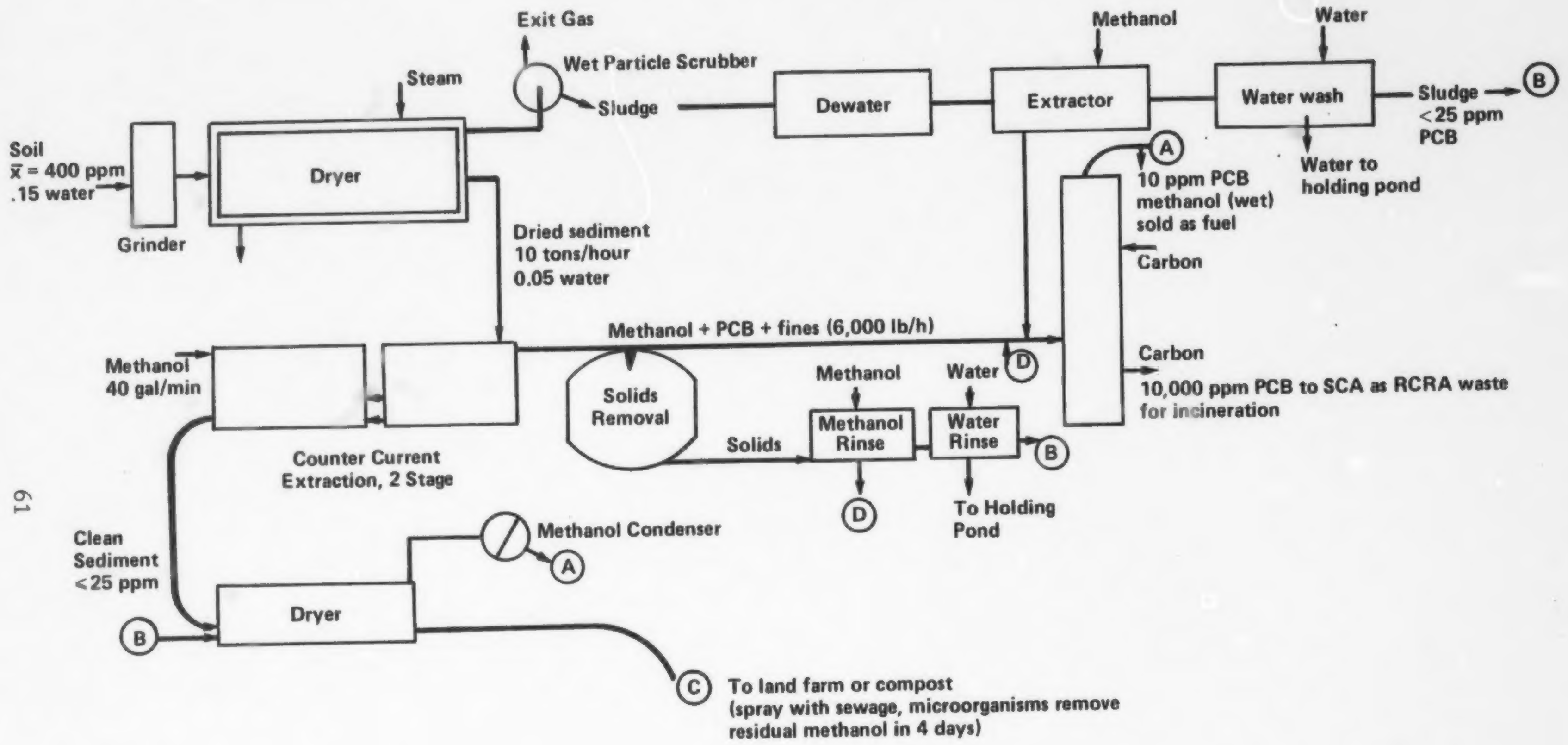

Exit Gas
Wet Particle Scrubber
Steam
Sludge
Dewater
Methanol
Extractor
Water
Water wash
Sludge
<25 ppm
PCB
B
Soil
$\bar{x}$ = 400 ppm
.15 water
Grinder
Dryer
Dried sediment
10 tons/hour
0.05 water
A
10 ppm PCB
methanol (wet)
sold as fuel
Water to
holding pond
Carbon
Methanol + PCB + fines (6,000 lb/h)
Carbon
10,000 ppm PCB to SCA as RCRA waste
for incineration
Methanol
40 gal/min
Solids
Removal
Methanol
Water
D
Methanol
Rinse
Water
Rinse
B
Solids
Counter Current
Extraction, 2 Stage
D
To Holding
Pond
Clean
Sediment
<25 ppm
Methanol Condenser
A
B
Dryer
C
To land farm or compost
(spray with sewage, microorganisms remove
residual methanol in 4 days)

Figure 11. Conceptual flow sheet, methanol extraction of PCBs from discussion with Robert Caron, EPA, Philadelphia regional office.

25 ppm. A two-stage extraction was used to reach the goals of 25 ppm for the treated sediment. Greater reduction (to less than 1 ppm) could be attained by adding additional stages to the extraction step, and this was taken into consideration in ranking the potential of this process.

4. The cleaned sediment was dried using a Hollow Flite dryer equipped with a condenser for the methanol carried in the exit gases. Air flow rates for drying were 14 m^3/min.

5. The dried, treated sediment was subjected to mild land farming, in which it was surface-spread and seeded with microorganism-containing waters. Residual methanol was found to be destroyed within 4 days.

6. The effluent from the extractors was heavily loaded with small particulate matter carried over from the sediments. About 2.7 Mg (6,000 lb) of fines was carried over for each 9 Mg (10 tons) of sediment treated. The solids were removed by settling. A centrifuge would probably be more appropriate for this step. It would give better separation and reduce carryover to the carbon adsorbers.

7. The separated particulates are combined with the main feed of cleaned sediments for drying and land farming.

8. The effluent, after removal of particulate matter, is treated by carbon adsorption to reduce its PCB content from about 10,000 to 10 ppm. This treatment produced a product suitable for resale as a fuel.

While further test and evaluation of this process will be required before its potential can be firmly assessed, it appears that the process is a viable alternative to landfill. The PCB removal efficiency attainable will depend upon the performance of the extraction system. There is, however, no reason why additional stages of extraction would not improve the efficiency so that the treated sediment would meet the goals of 1 to 5 ppm residual PCB.

The drying operation contributes to the cost and creates the need for pollution controls, particulate recovery, and handling of the particulate as a toxic waste. It may be possible to avoid drying if the process can be driven by 50 percent methanol, such as would be generated if the sediments with 15 percent moisture were treated without removal of the water. One single-stage wash would yield a diluted methanol solution. Then countercurrent extraction could be applied to the sediments.

The extraction operation has a substantial particulate carryover problem, which will need to be addressed for other extraction processes as well.

5.2.1.3.1 Cost--Based on the conceptual process and the experience thus far, the process is estimated to cost $400 to $514/m^3, including dredging and transport costs (Caron 1985). In the field application, methanol was purchased at $0.69/gal ($0.18/L) and resold at $0.23/gal ($0.06/L).

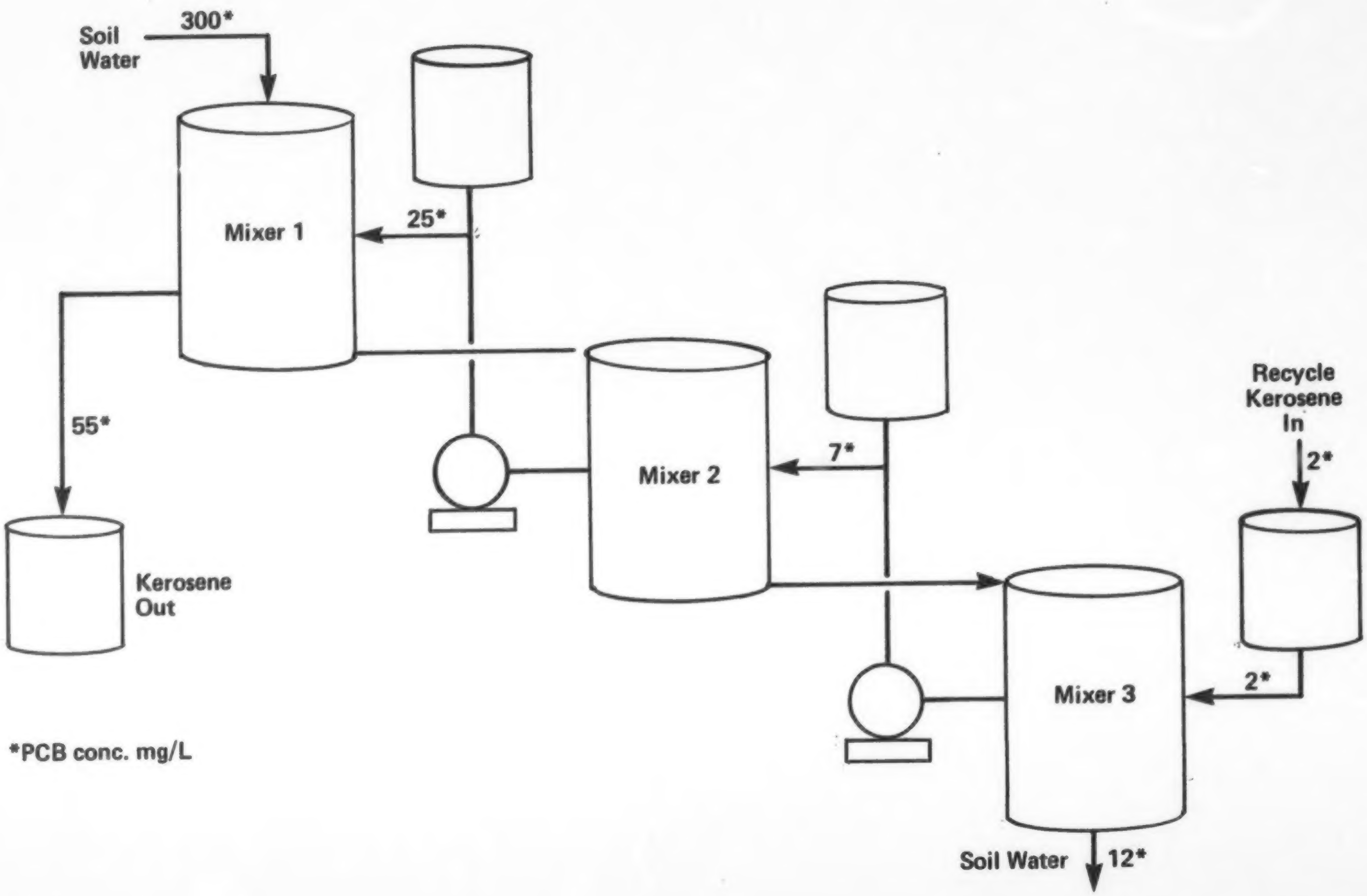
5.2.1.4 Soilex Solvent Extraction Process--

"Soilex" is a process in development at the Oak Ridge National Laboratory (M. B. Saunders 1985). Kerosene and water were determined to be the solvent of choice. Kerosene can be recovered for recycle by stream-stripping. Soil-to-water ratios of 3 to 5 and soil-to-kerosene ratios of 3 to 5 were found to be best. No difference in extraction performance could be determined between 15- and 30-min mixing times. The kerosene retention in the soil was about 25 vol percent. A three-stage batch pilot unit operating with a 6-to-1 volume ratio experienced soil feed PCB concentrations of 180 to 350 ppm and discharge soil levels of 6 to 9 ppm. Lower soil values could be obtained using additional stages.

5.2.1.4.1 Selection of solvent mix--The soil tested also had a high concentration of oils and tars, resulting in a total organic carbon concentration of 10 to 20 percent. The PCB and oil were solubilized using the kerosene leaching solvent. Water was also added to the solvent mixture to help break up the soil particles.

The extent of PCB extraction from the soil as a function of soil-water-kerosene ratios and the mixing times was determined to define areas of acceptable operation. To minimize operation and equipment costs, the water and kerosene-to-soil ratios must be as low as possible. The data indicate that a water-to-soil ratio less than 1.0 and/or a kerosene-to-soil ratio less than 1.0 result in a mixture that does not have enough fluid to allow for adequate mixing and is therefore not acceptable for operation. A ratio of water-to-soil and kerosene-to-soil greater than 5.0 requires processing a high volume of material. A ratio of 3.0 to 5.0 for the water-soil ratio and kerosene-soil ratio resulted in a system having good hydraulic mixing characteristics and yielded a PCB leaching percentage of 84 percent.

5.2.1.4.2 Description--The pilot plant (Figure 12) consists of three stages of mixing equipment. The plant is operated in a countercurrent mode;


Soil
Water
300*
Mixer 1
25*
55*
Kerosene
Out
Mixer 2
7*
Recycle
Kerosene
In
2*
Mixer 3
2*
Soil Water
12*

*PCB conc. mg/L

Figure 12. Soilex pilot plant.

soil and water were added to stage 1 and clean kerosene to stage 3. Each mix tank has a 200-L capacity and an air-driven mixer. An interstage solvent pump and a 120-L solvent-hold tank allows the kerosene to be transferred in a countercurrent mode. The distillation packed column system was 7.56 cm in diameter by 2.4 m long, with an 18-L steam-heated reboiler and product condenser (Figure 13). The distillation unit was used to steam-strip the recyclable kerosene from the other oils and PCB.

5.2.1.4.3 Operation--The pilot plant is a 1-day batch-cycle operation. Each day the solvent is pumped from each of the three mix tanks to their solvent-hold tanks. The water-soil mixed phase is transferred by gravity to the next stage, untreated soil and recycle water to stage 1, and fully treated soil and water are discharged from stage 3. The kerosene is then drained from the hold tanks to the next lower numbered mixer. The transfer operation takes about 3 h to complete. The tanks are mixed for 4 h. Samples removed from the mix tanks at 30-min intervals indicate that the mix tanks are at steady-state after 90 min. After mixing has been stopped, the mix tanks are allowed to phase-separate for 16 h, thus consuming 1 d per batch.

5.2.1.4.4 Performance--The pilot plant was operated for 19 batch days. Successful steady operation was obtained after 4 d. A 25-L batch of PCB and oil from the solvent-extraction pilot plant was steam-stripped to recover the kerosene in 3 h using 500 mL/min of water feed to the boiler operating at 110 °C. Twenty-two liters of kerosene were recovered at a PCB concentration less than 5 mg/L. The PCB was concentrated to 15 mg/L (6 to 9 ppm).

Since the process operates best with from 42 to 45 vol percent water present, it offers the advantage of accepting wet sludges for treatment without drying. The drying operation, with its attendant pollution controls is obviated. The process requires simple stirred tanks for extraction, as projected from the pilot plant. However, each batch of sediment requires 3 days (72 hours) for treatment. After that, it is discharged holding 25 to 30 weight percent adsorbed kerosene. The sediment-solvent mixes were stirred for only 90 min of each 24-h cycle, and the cycle was repeated three times. Most of the processing time was spent in allowing the solid phase to settle and the liquid phases to separate. More time- efficient separation techniques need to be tested for applicability to the separation step.

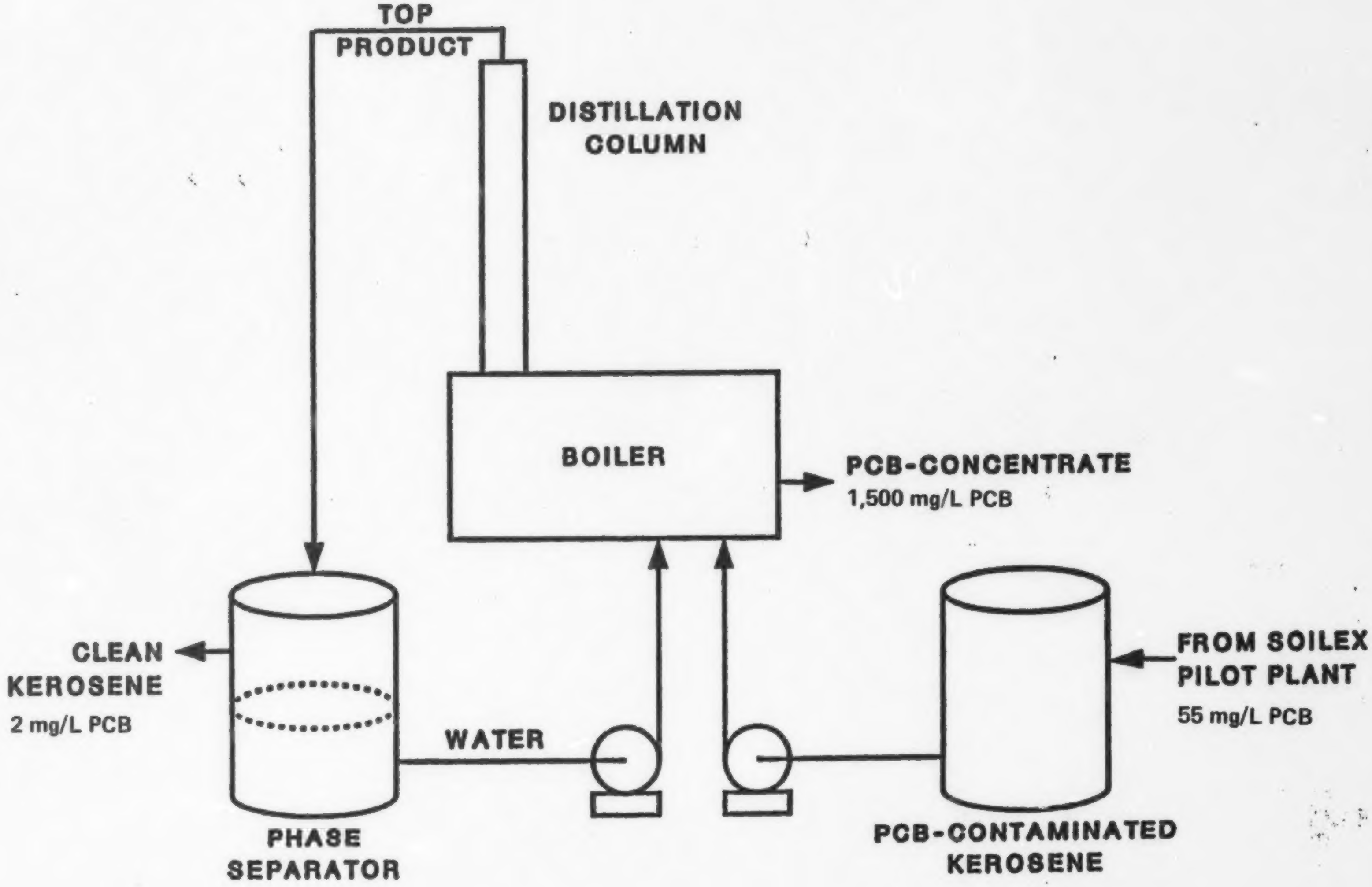

TOP
PRODUCT
DISTILLATION
COLUMN
BOILER
PCB-CONCENTRATE
1,500 mg/L PCB
CLEAN
KEROSENE
2 mg/L PCB
WATER
PHASE
SEPARATOR
FROM SOILEX
PILOT PLANT
55 mg/L PCB
PCB-CONTAMINATED
KEROSENE

Figure 13. Soilex steam distillation unit.

The selected water, kerosene, and soil ratios gave good hydraulic mixing characteristics and yielded "a PCB leaching of 84 percent." Since the soil tested contained from 10 to 20 percent oils and tars with 300 to 600 ppm PCBs, the solvent mix test dealt with PCB-containing oils spilled onto the soil. It is not clear how the PCBs were distributed, how much was dissolved in oil films surrounding the soil, or how much was adsorbed directly into the soil. Tests using several more stages of extraction would be needed to demonstrate that the extraction could, by use of more stages, achieve the 1- to 5-ppm residual PCB levels desired. Studies of kerosene extraction at EPA and at New York University may resolve this problem.

The process generates an RCRA waste (concentrated PCBs) requiring treatment and disposal.

5.2.1.4.5 Cost--A rough cost estimate by RTI, based on increasing the number of extraction stages to achieve desired background levels of PCBs in the treated soil, is: $856 to $913/m^3. This includes dredging, transportation, treatment, and redeposition of the treated sediments.

5.2.2 Vitrification

5.2.2.1 Principles--

Vitrification stabilizes radioactive-contaminated soils by melting. Large-scale tests have demonstrated the vitrification of 300 Mg per setting (Timmerman 1985). At the high temperatures created (>1700 °C), the process pyrolyzes organic materials. The products of pyrolysis diffuse to the surface and combust. Any off-gases must be collected, monitored, and treated. Remaining ash, along with other noncombustible materials, dissolves or becomes encapsulated in the melt. Natural convective currents within the molten mass help distribute the stabilized materials more uniformly. The molten soil or sediment is allowed to cool to a durable glass and crystalline form.

5.2.2.2 Battelle In Situ Vitrification Process--

In situ vitrification (ISV) is a patented process developed at Battelle Pacific Northwest Laboratory for the U.S. Department of Energy as an in-place stabilization technique (Timmerman 1985). Submerged sediments would be dredged before being subjected to this treatment. In evaluation of its potential application to soils contaminated with PCBs, an engineering-scale in situ vitrification test with PCB-contaminated soil has been performed for the Electric Power Research Institute to determine the fate of PCBs and their byproducts when the process is applied.

5.2.2.2.1 Description--The process tested on a small scale is shown schematically in Figure 14.

1. A 20-cm-diameter by 30-cm-deep zone of loamy-clay soil, containing 500 ppm PCBs was centrally located in a sealed metal container. The contaminated soil was surrounded by noncontaminated soil and was 25 cm beneath the surface.
2. Four cylindrical molybdenum electrodes were set on a 23-cm square to surround the contaminated soil. The electrodes extended to a depth of 61 cm.
3. A path for electric current was established by placing a small amount of graphite and glass frit mixture between the electrodes on the soil surface.
4. Off-gases were collected and passed through a dual-stage activated carbon filter to contain any PCBs or decomposition products released. Online grab samples of exit gases were taken from a sample port. The samples were analyzed for chlorine and hydrogen chloride.
5. Electric power was applied for a 6-hour period. A vitrified block (220 kg) and 0.14 m^3 was produced. The melt extended to a depth of 81 cm.
6. In addition to sampling off-gas emissions, residues in off-gas lines and containment equipment, the migration of PCBs into the surrounding soil, and the residual level of PCBs in the vitrified block were monitored.

5.2.2.2.2 Performance data--Online grab samples revealed less than detectable quantities of chlorine and hydrogen chloride (<0.33 ppm and <0.2 ppm, respectively). Data from off-gas release and soil container smears provided the most quantitative values on the release from the melt during and after processing. Information collected from the adsorption tubes and the smear sample extractions indicated a 4.4-mg total off-gas emission, 1.1 mg of which was deposited on container surfaces. These off-gas releases accounted for 0.05 wt% of the initial PCB quantity, corresponding to a greater than 99.9 percent thermal destruction and removal efficiency for the ISV process.

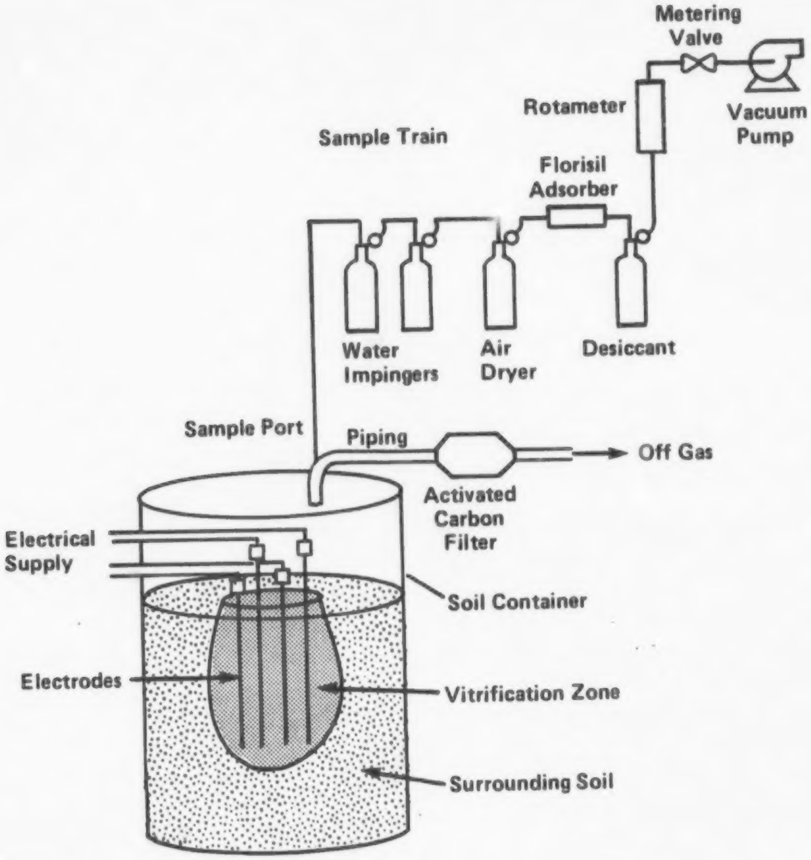

Metering Valve
Rotameter
Vacuum Pump
Sample Train
Florisil Adsorber
Water Impingers
Air Dryer
Desiccant
Sample Port
Piping
Off Gas
Activated Carbon Filter
Electrical Supply
Soil Container
Electrodes
Vitrification Zone
Surrounding Soil

Figure 14. Engineering scale vitrification system and sample locations.

This does not include the removal efficiency of the off-gas system; therefore, a system DRE cannot be calculated from the available data. Activated carbon filters can effectively contain any of the off-gas emissions.

Analyses of the florisil adsorber also indicated a small amount of furan (PCDF) and dioxin (PCDD) generated in total quantities of 0.4 μg and 0.1 μg, respectively. Only the tetra and penta isomers of the PCDF were detected, and only the hepta and octa isomers of the PCDD were detected. These small quantities are less than the reported amounts typically generated from a PCB fire and do not represent a hazardous operational concern.

The vitrified mass showed no detectable residual level of PCB, which is to be expected considering the high processing temperatures. Also, no PCB contamination was detected in the majority of soil surrounding the vitrified block, indicating that migration outside the vitrification zone was not a significant problem. A few samples directly adjacent to the block contained measurable concentrations up to 0.7 ppm, which is acceptable. These results indicate that the vitrification rate must be higher than the diffusion rate of volatilized PCBs in soil, thus overcoming migration away from the hot molten mass.

The product of this process is a solid glass and crystalline block. This form may be more costly to redeposit. There may be fewer options than would be available for ordinary sedimental material. The nature and extent of emissions from the melt would likely vary from one type of sediment to another. Sediments containing significant amounts of organic matter would lose all of it by pyrolysis and vaporization. To conserve energy usage, sediments high in moisture should be dried prior to treatment.

5.2.2.2.3 Cost--The cost of using the vitrification as a technique for in-situ treatment has been estimated by the developers. The estimate includes expenses from four categories: site preparation and closure activities, annual equipment charges, operational costs, and consumable supplies including electrical power and molybdenum electrodes. These costs are estimated to be between \$150 and \$330/m^3 depending on electrical power rates and soil moisture content. Soil moisture content increases the cost by requiring more energy and time to vitrify a given volume of contaminated soil because the water in the soil must be evaporated. The total cost of using this approach requires, for submerged sediments, the addition of dredging, transportation, and redeposition costs.

The solidified blocks of treated sediment could not be disposed of by land treatment. If treated at a hazardous waste facility, they could be landfilled there. The cost of such disposal would probably be the regular charge for hazardous waste disposal, \$260 - \$490/m^3. The treated material is estimated to be eligible for delisting, however, and redeposition at a lower cost should be possible. Given that the physical form of the treated sediments will limit somewhat the available locations for its redeposition, a cost of \$72/m^3 has been estimated. This cost is less than that of controlled, managed land treatment (\$111) since the material would require no control or management. It is greater than the \$33/m^3 cost of short-term land treatment. The overall cost estimate is thus:

$$\text{Cost, \$/m}^3 = (\text{\$20 dredging}) + (\text{\$13 - \$126 transporation}) + (\text{\$150 - \$330 treatment}) + (\text{\$72 redeposition})$$

$$= \text{\$255 to \$548.}$$

5.3 BIOLOGICAL TECHNOLOGIES

5.3.1 Microorganisms and Enzymes

5.3.1.1 Principles--

Biological technologies for PCB treatment include the use of free microbes or their enzymes. The microbes may be bacteria or fungi and may act aerobically (or anaerobically) or facultatively. They may be indigenous microorganisms, conventional chemical mutants, or recombinant microorganisms. Their action may result in partial or total degradation of the PCBs. Total degradation, termed mineralization, occurs when the metabolic products are CO_2, H_2O, and HCl. Their action may take place within the cell (bacteria) or external thereto (fungi).

Enzymes may be applied as free-flowing solutions or bonded to a solid substrate. The use of enzymes alone has great conceptual potential but has not progressed very far at this time.

Thirty-four bacterial strains and five fungal strains have been shown to have varying degrees of competence in degrading PCBs (Unterman et al. 1985; McCormick 1985; Rochkind et al. 1985, Bumpus et al. 1985, Isbister et al. 1984). These microorganisms metabolize PCBs using enzymes specific to the strain. Since most enzymes are notably specific in their actions, different enzymes catalyze the reaction of different PCB isomers (termed cogeners in the biotechnology literature). In some cases, the cogener may be metabolized only partially by a particular species, and a product (e.g., a chlorobenzoate) may accumulate. In a parallel situation, another species may be able to metabolize that product further, although the second species may lack enzymes needed to metabolize the parent PCB. By themselves, neither species could mineralize the cogener. However, a mixed culture might act in concert mineralizing the product resulting from metabolism of the substrate by the other species. A consortia of more than two species may be required to mineralize a substrate and the effective species may be bacteria, fungi, or a mixture of the two.

Some cells cometabolize PCBs; that is, they metabolize a PCB cogener while obtaining their carbon and energy from other sources. Such metabolism may be partial or complete and depends upon enzymes already active in the cell.

Biological technologies include a very broad spectrum of potential capabilities, many aspects of which are being explored. True measures of their ultimate capabilities for PCB-destruction cannot yet be made. In the following sections, recent developments in mutant and enzyme technology are described.

5.3.1.2 Indigenous and Conventional Chemical Mutants--

Indigenous and conventional chemically mutated microorganisms (those found growing naturally in diverse PCB-containing soils and sediments) have been isolated, identified, and tested for PCB-degradation capability using an assay mixture containing five types of cogeners selected to pro- vide different resistances to enzyme attack (Bedard et al. 1985). The assay mixture was composed of the following types, selected from the over 100 different cogeners:

1. Single-ring substitution:	2,3 Dichlorobiphenyl
2. Double para substitution no free 3,4 sites:	4,4' Dichlorobiphenyl

3. No free 2,3, sites: 2,5,2',5' Tetrachlorobiphenyl

4. No adjacent unchlorinated sites: 3,5,3',5' Tretrachlorobiphenyl

5. Two or more ortho chlorines, steric hindrance: 2,6,2',6' Tetrachlorobiphenyl

Table 6 lists the results obtained using 25 strains, including 15 isolates and 11 unidentified field isolates (e.g., H337 is an unidentified gram-negative organism isolated from Hudson River sediments).

The results identify *Alcaligenes eutrophus* H850 and *Pseudomonas putida* LB400 as the best microorganisms, both being able to degrade 13 test cogeners 80 to 100 percent.

Table 7 lists 10 additional strains of bacteria studied by different investigations. Of these, the *Arthrobacteria* degraded the most PCB cogeners. The table also lists 5 fungi that have been studied. To date, the fungi show less effectiveness than the bacteria (2 percent vs 80-100 percent).

The degradative pathways and cogener preferences differ among the microorganisms. Many bacteria oxidize PCBs via chlorobenzoic acid intermediates and often accumulate the chlorobenzoate products (Furukawa, 1982). The major pathway proposed for *A. eutrophus* H850 involves a dioxygenase that preferentially attacks at carbon positions 3,4 (Unterman et al. 1983). In contrast, *Corynebacterium sp* MB1 probably employs a more common 2,3 dioxygenase mechanism.

Genetics studies of PCB-degrading bacteria have demonstrated that some of the effective strains contain one or more plasmids (Unterman et al. 1985). Plasmids are stable extrachromosomal circular double-stranded DNA replicons that are inheritable but are also dispensable. Mutants of H850 that have lost their plasmid have also lost the ability to metabolize PCBs.

Mutations that living cells may undergo alter the genetic message. Sometimes the alterations in the DNA code may lead to alteration of the cell's metabolism. Some mutations allow the cell to survive in the presence of potentially toxic compounds. In other cases, the cell acquires the ability to use previously unsuitable substrates. Some agents, including UV light, some

TABLE 6. PCB DEGRADATION BY BACTERIAL STRAINS: PERCENT DEGRADATION BY COGENER
(RAPID ASSAY TEST)

Bacterial strain		PCB cogener (%)																	
		2,3	2,4'	2,5,4'	2,2'	2,3, 2',3'	2,5,2'	2,3, 2',5'	2,4,5, 2',3'	2,5, 3',4'	2,3,4, 2',5'	4,4'	2,4,4'	2,4, 3',4'	2,4, 2',4'	3,4, 3',4'	2,5, 2',5'	2,4,5, 2',5'	2,4,5, 2',4'.5'
Acidovorans group	H702	80-100	80-100									80-100	80-100						
Pilol		80-100	80-100		60-79	20-39	20-39					80-100	80-100	20-39					
Alcaligenes eutrophus	H850	60-79	80-100	80-100	80-100	80-100	80-100	80-100	40-59	80-100	80-100	60-79	80-100	40-59	80-100	40-59	80-100	80-100	40-59
Alcaligenes faecalis	Pi 434	80-100	80-100		20-39							80-100	40-59						
Corynebacterium	sp M81	80-100	80-100	80-100	80-100	80-100	60-79	80-100	80-100	40-59		80-100	80-100	80-100					
Pseudomonas	sp Pi 939	80-100	80-100									60-79	20-39						
	H 1138	80-100	80-100									80-100	80-100						
Pseudomonas testosteroni	H128	80-100	80-100	60-79	80-100	80-100	20-39					80-100	80-100	40-59					
	H338	80-100	80-100	80-100	80-100	60-79	80-100	40-59	40-59				60-79		60-79				
	H430	80-100	80-100	80-100	80-100	80-100	60-79					80-100	80-100	40-59					
Pseudomonas cepacea	RJB	80-100	80-100	40-59	20-39	20-39						80-100	60-79						
	Pi 704	80-100	80-100	40-59								80-100	80-100	20-39					
	H 201	80-100	80-100									80-100	80-100						
Pseudomonas putida	LB400	80-100	80-100	80-100	80-100	80-100	80-100	80-100	40-59	80-100	80-100	60-79	80-100	40-59	80-100	40-59	80-100	80-100	40-59
	Pi 384	80-100	80-100									40-59							
	Pi 483	80-100	80-100									60-79	60-79						
	991	80-100	80-100	60-79								80-100	80-100	40-59					
	F39	80-100	80-100	60-79	80-100		40-59					80-100	80-100						
	H19	80-100	80-100	80-100	20-39	20-39						80-100	80-100	60-79					
	E12	80-100	80-100	40-59	80-100	60-79						80-100	80-100	20-39					
	H337	80-100	80-100	60-79	80-100	80-100	20-39					80-100	80-100	20-39					
	Pi 432	80-100	80-100	80-100	80-100	80-100	40-59					80-100	80-100	40-59					
	H 125	80-100	80-100	80-100	80-100	80-100	40-59					80-100	80-100	40-59					
	E13	80-100	80-100	80-100	80-100		20-39					80-100	80-100	40-59		40-59			
	Pi 918	80-100	80-100	80-100	80-100	60-79	80-100	20-39	40-59				60-79		60-79				

TABLE 7. PCB DEGRADATION BY BACTERIAL AND FUNGAL STRAINS: LONGER TESTS

	Bacterial strains							
	Acinobacter sp P6	Alcaligenes BM2 (3-day test)	Alcaligenes sp Y42	Achromobacter sp PCB	Arthrobacter w plasmid	Facultative anaerobe B206	Beijerinckii	Klebsiella (cogener not specified)
Reference	McCormick, 1985	Rochkind et al., 1985	Rochkind et al., 1985	Rochkind et al., 1985	Isbister et al, 1984	Rochkind et al., 1985	McCormick, 1985	McCormick, 1985
2,3		80-100%			ND			
2,4'		80-100%			ND			
2,5,4'								
2,2'		80-100%			ND			
2,3,2',3'	ND							
2,5,2'		80-100%						
2,4,4'	ND	80-100%						
3,4,3',4'								
4,4'		80-100%			ND			
2,4,5,2',4',5'								
2,5								
3,4,3'								
3,4								
4	ND		ND	ND	ND	ND	ND	
2,3,2'								
2,3,4'								

(continued)

ND=percent not determined.

TABLE 7 (continued)

	Bacterial strains (continued)		Fungal strains				
	Norcadia 10603 (2-week test)	*Pseudomonas* *sp* 7509	*Candida tropicalis* (cogener not specified)	*Cunninghamella echinulata* (Thaxter)	*Cunninghamella elegans* (cogener not specified)	*Phanerochaete chrysosporium* (white rot fungus)	*Rhizopus japonicus*
Reference	Rochkind et al. 1985	Rochkind et al. 1985	McCormick 1985	Rochkind et al. 1985	McCormick et al. 1985	Bumpus et al. 1985	Rochkind et al. 1985
2,3	60-79%						
2,4'	60-79%	ND					
	60-79%						
2,5,4'	(10-week test)						
2,2'							
2,3,2',3'							
2,5,2'							
2,4,4'							
3,4,3',4'						2.0%	
4,4'							
2,4,5,2',4',5'						2.0%	ND
2,5				ND			
3,4,3'	60-79%						
3,4	60-79%						
4							ND
2,3,2'	60-79%						
2,3,4	60-79%						

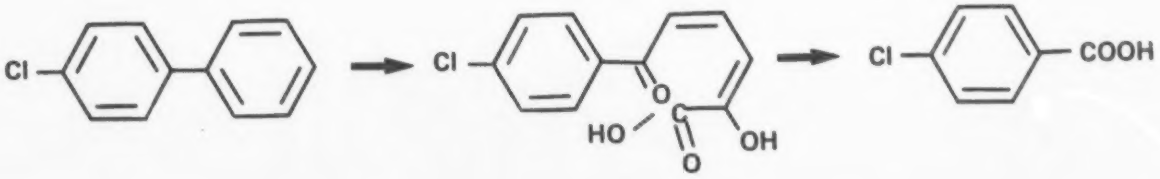
ND=percent not determined.

kinds of radiation, and some chemical agents, cause increased mutagenesis. These mutations are characterized by being randomly distributed across the DNA. Mutations can be selected by applying selective pressures to a population, creating an unfavorable environment in which only those cells that have mutated so as to adapt to the environmental situation will survive. Such adaptation may take months before the altered population is large enough to be observed.

5.3.1.3 Enzyme Mechanisms--

Limited studies on the degradation of specific chlorinated biphenyl compounds by pure strains of bacteria have established some general features of PCB metabolism (Rochkind et al. 1985). A few strains have been shown to mineralize some chlorinated biphenyls. In most cases, bacteria can degrade one ring of a chlorinated biphenyl but are unable to degrade the resulting chlorinated benzoates. These compounds accumulate in pure cultures. Other strains have been shown to be capable of completely mineralizing chlorinated benzoates (e.g., the hybrid strain of Pseudomonas sp B13 carrying the relatively nonspecific oxygenase of P. putida mt-2 carried on the TOL plasmid). Mixed cultures of bacteria have been shown to mineralize PCBs with four or fewer chlorines per molecule. More heavily substituted PCBs appear to resist degradation to a greater extent.

The mechanism of hydroxylation of PCBs by bacteria has not been elucidated, nor have the enzymes mediating the steps in the proposed pathways been isolated. Two pathways have been proposed. The first involves initial hydroxylation in the 2,3-position of the less substituted ring, followed by meta cleavage and subsequent degradation of the aliphatic portion of the molecule to form substitiated benzoic acids. Chlorines on the aliphatic carbons are lost during this process.



However, this may not be the mechanism for degradation of PCBs substituted in all the ortho positions. A second pathway, based on the action of a monooxygenase in bacteria has been proposed after discovery of 4-hydroxy-4'-chlorophenyl in extracts of bacteria cultures incubated with 4-chlorobiphenyl (Catelani et al. 1971). More evidence corroborating this mechanism is needed. Unterman et al. (1985) proposed that the major pathway of PCB metabolism in A. eutrophus H850 utilizes a dioxygenase that preferentially attacks at carbon positions 3,4; while Corynebacterium sp. MB1 probably employs a more common 2,3 dioxygenase.

Limited evidence on fungal metabolism of PCBs indicates activity of a monooxygenase.

Little has been done to prepare or work with enzymes alone, separated from the organisms, despite the conceptual attractiveness of the approach. The separation processes for PCB-degrading enzymes are yet to be developed. Some enzymes may be cell wall bound, requiring special handling in their preparation. At present, little is known concerning the use of enzymes alone for PCB decontamination of sediments.

5.3.1.4 Bio-Clean Process--

The Bio-Clean process is a biological treatment process developed by Bio-Clean, Inc., Bloomington, Minnesota. It has been well demonstrated for PCPs. It requires further testing with, perhaps, the use of some additional strains of microorganisms to bring it through the pilot stage for PCBs. It is listed here as a representative bio-process that has potential application and can be made available commercially. It does not require pretreatment to dewater sediments, and it does not appear to generate any RCRA wastes or emissions. Bio-Clean has proposed to process the sediments as they are dredged, using a series of nine floating barges with processing units on board. This would eliminate the need for sediment transport and replacement, and would eliminate the associated costs.

5.3.1.4.1 Description--The process involves two steps: (1) extraction, sterilization, and solubilizing the contaminants using high pH and temperature, and (2) bacterial destruction of the contaminant. These steps generally require 3 days. Standard digesters that can handle 22 to 28 m^3 of sediment (dry bases) are used in sets of three to provide a daily capacity in multiples of 22 to 28 m^3/day. (Larger units are discussed later in this section). Figure 15 is a flow diagram of the process as applied to contaminated soils. The processing cycle requires four steps:

1. Contaminated sediment is charged to the digester, in slurry form if so received. The final digester charge will be approximately 2/3 water and 1/3 solids. The charge is made alkaline with sodium hydroxide (or other alkaline hydroxide), then heated to approximately 82 °C, at which temperature it is held for one hour. The mix is agitated to promote solubilization of the PCBs.

2. After the extraction, the slurry is cooled to 30 °C, neutralized and inoculated with a selected microorganism(s) to initiate decontamination. The slurry is kept under these conditions for 48 to 72 h as required, until the desired degradation has been attained. The exact time requirements must be determined by tests for each particular decontaminant. The degradation is an aerobic process and uses sterile filtered air for oxygen.

3. A treated batch of sediment is discharged to a dewatering pit where the sediment is separated for redeposition. The material is sampled and tested to determine the concentration of residual PCB prior to its relocation. The water is also analyzed for PCBs and thus disposed of in a manner suitable for the particular site (e.g., through sanitary sewer systems, storm sewer systems, or percolation into the ground or recycle).

4. At the end of the decontamination period, the cycle begins again at 1.

5.3.1.4.2 Residual PCB concentration--In laboratory tests, selected PCB cogeners have been reduced to 10 ppb in 48 to 72 hours. The process utilized *Arthrobacteria sp* under aerobic conditions. Further testing must be done using the specific sediment of interest to determine the specific capabilities for given PCBs. Bio-Clean is equipped to do screening tests. However, a more extensive test and development study is needed to assess the potential of the process adequately. In such tests, other species of microorganisms that have shown broad capabilities for degrading many PCBs could be tried (e.g., *Alcaligenis eutrophus* and *Pseudomonas putida* LB8400).

5.3.1.4.3 Conditions/limitations--The organisms are naturally occurring. Their degradation products have been shown to be CO_2, NaCl and bacterial cells. Supplementary nutrients (ammonia nitrogen, phosphorus, and potassium) would be required with some sediments.

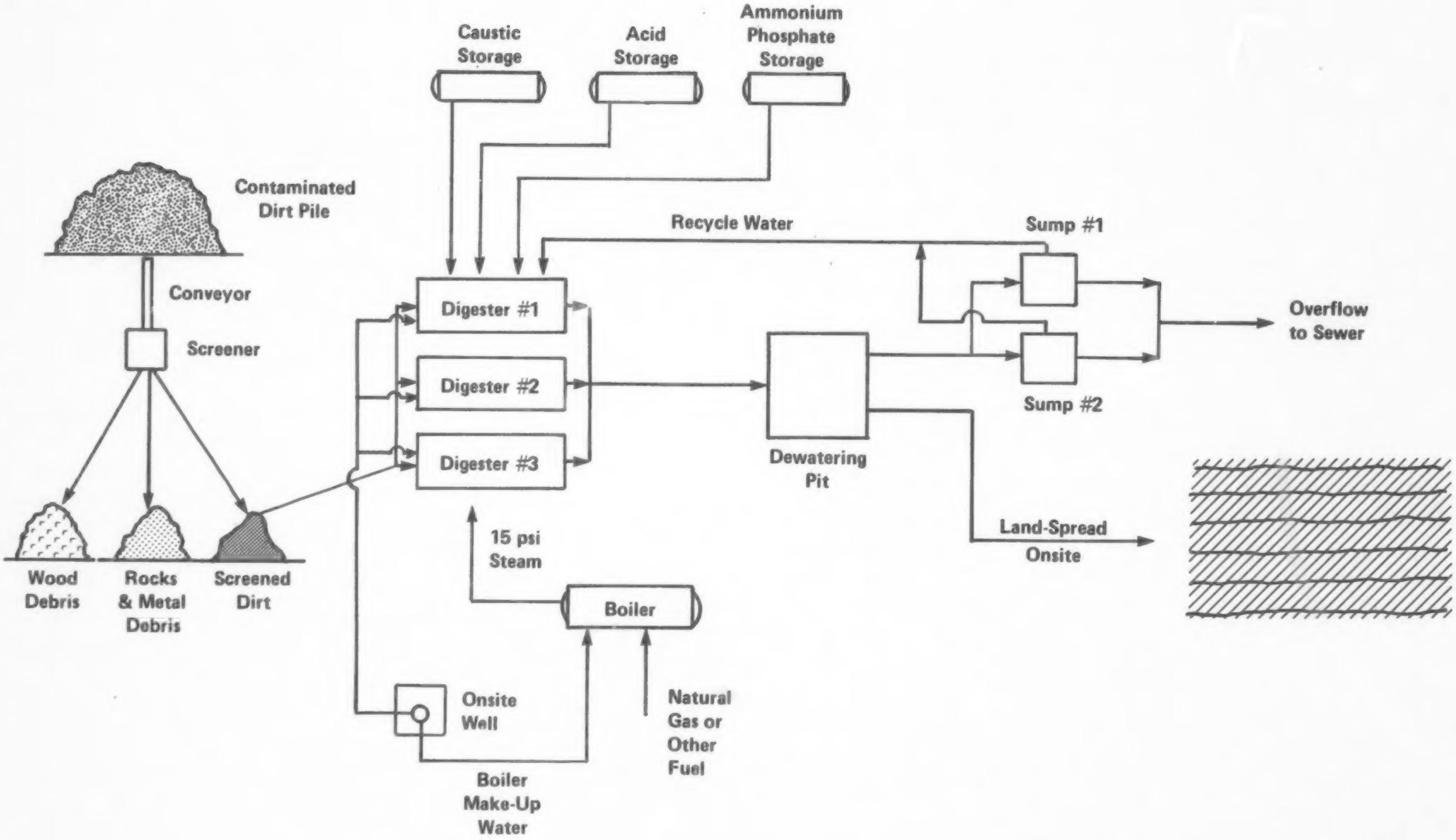

Caustic Storage
Acid Storage
Ammonium Phosphate Storage
Contaminated Dirt Pile
Conveyor
Screener
Wood Debris
Rocks & Metal Debris
Screened Dirt
Digester #1
Digester #2
Digester #3
Recycle Water
Sump #1
Sump #2
Overflow to Sewer
Dewatering Pit
Land-Spread Onsite
15 psi Steam
Boiler
Onsite Well
Boiler Make-Up Water
Natural Gas or Other Fuel

Figure 15. Bio-clean process applied to contaminated soils.

Very high PCB concentrations (e.g., >300 ppm) inhibit the degradation process. It may be slowed down or halted. Contaminated sediments may vary significantly in PCB loading. To avoid inhibition of the process, the sediments could be slurried in a premix tank for blending to control PCB levels.

5.3.1.4.4 Availability--Laboratory-scale and pilot-scale (760 L) evaluation facilities are available at Bio-Clean. Pilot tests could be carried out under sponsorship.

5.3.1.4.5 Scale-up--For large-scale cleanups, large horizontal tank digesters (each handling 540 Mg of sediment per charge) or floating barge tankers would be used. These would be used in sets of three. Each set could treat an estimated 115,000 m^3/year of contaminated sediment. Three sets would treat the estimated 382,000 m^3 of contaminated sediments in the Hudson River in 13 months or less with large barge tankers (based on 355 days operation per year).

5.3.1.4.6 Cost--The estimated cost of treatment using the Bio-Clean process on floating barges is \$191 to \$370/m^3. This includes dredging at \$20/m^3, and treatment costs at \$171 to \$350/m^3.

5.3.1.5 Sybron Bi-Chem 1006 PB/Hudson River Isolates Process--

The Sybron process is a conceptual process still in the laboratory scale (Kopecky 1985). Information obtained from the company was very limited, and its evaluation is correspondingly limited. The process may be able to operate under both aerobic conditions or anaerobic conditions with facultative aerobes and supplements of nitrates. Further studies to define an anaerobic process concept and principles have been proposed (Kopecky 1985; and Rhee 1985a).

5.3.1.5.1 Description--This process has not been developed sufficiently to permit a description in terms of unit operations. Information provided by Sybron includes tests of their Bi-Chem 1006 PB for removal of PCBs from a municipal sewage sludge. (Status Report New York Department of Environmental Conservation, May 21, 1985). The sludge contained 100 ppm of PCBs. After treatment for an unspecified time with Bi-Chem 1006, the PCBs were reduced to undetectable levels (<1 ppm). Hudson River sediments were also treated with

Bi-Chem 1006. In 6 weeks of incubation, the concentrations of a monochlorinated biphenyl and a dichlorinated biphenyl were reduced by half. When the Hudson River isolates were added to the Bi-Chem 1006, the sediment concentrations of these particular biphenyls reduced slightly more than half in the same incubation period. However, a second dichlorinated biphenyl was not reduced at all during this period by either treatment.

5.3.1.5.2 Application--The conditions under which microorganism activity occurs (anaerobic or facultative) would permit two potential modes of application to submerged sediments: in situ decontamination and treatment under containment of dredged sediments. In situ decontamination would involve the injection and mixing of microorganisms and nutrients in the submerged sediments, and, perhaps, maintaining them in place for rather long periods of time. As a treatment under containment, the organisms and nutrients would be fed from a mass culture system to sediments being pumped to holding sites. Effluents from the holding site would be subject to treatment for leached nutrients and other components from the inoculation process. Proof-of- principle laboratory tests for in situ treatment have been proposed. Engineering for in situ application has not been addressed. The parameters for mass culture and the feed system for use in conjunction with the sediment containment site are not currently available for assessment.

The possibility of an in situ treatment process inherent in this approach is a subject for fundamental research. Until the concept is more clearly defined, the approach cannot be assessed. The advantages of in situ treatment are obvious, however.

Data needs relate strongly to the engineering requirements of such a process. The required doses of organisms and nutrients must be determined and related to PCB degradation efficiency. The scale of resources needed to treat 300,000 m^3 of contaminated sediment needs to be determined. The extent of leaching of nutrients, and of dissolution of toxic substances, needs to be estimated if the system is to be an open containment type.

Cost estimates for this application process could not be made, due to the limited available information..

5.3.1.6 Composting--

Aerobic and anaerobic composting of PCB-contaminated soil has been studied on a laboratory scale by Isbister, Anspach, and Kitchens (1984). Experiments were carried out with soil that was intentionally spiked with PCBs (Aroclor 1242). Mason jars were used to contain the compost materials. For the aerobic composts, warmed air was first drawn through a sodium hydroxide trap to remove any CO_2 and then through a water trap to humidify the air and remove any caustic material. The scrubbed air was then drawn through the compost materials. The atmosphere above the compost was continually drawn out through sulfuric acid, sodium hydroxide, and activated carbon traps to remove any gaseous biodegradation products. The dead traps prevent contamination of the composts of individual gas traps in case of vacuum failure. For the anaerobic composts, the initial NaOH scrubbing trap was eliminated. The anaerobic composts were initially flushed with nitrogen to remove oxygen from the system, and they were flushed every 3 to 4 d thereafter to change the atmosphere in the composting vessels.

Each compost was made up of 23.7 g of alfalfa hay, 24.7 g Purina Sweetena Horsefeed and 5 g of lakeland soil (a total of 50 g dry wt.). The soil was spiked to yield 2,000 mg/kg of Aroclor 1242 in the total compost (dry wt. basis). The compost materials were thoroughly mixed, and the composting process was started by addition of sufficient water (containing primary effluent and horse manure) to give the compost a 60-percent moisture content. The composting apparatus was then placed in a 55 °C incubator and attached to the vacuum system. The temperature of each compost was monitored daily by means of a thermocouple placed within the compost materials.

The composts were sacrificed after 2- and 4-week intervals, and each compost was examined for appearance and smell. The pH was determined on a portion dispersed in water. The remainder of each sample was dried 24 h at 60 °C and ground with a hammer pulverizer to 18 mesh. The powder was then mixed. Two subsamples were Soxlet-extracted with a mixture of benzene, acetone, hexane, and methanol. (The extraction efficiency of Aroclor 1242 from uncomposted materials ranged from 83 to 89 percent.) Each extract was diluted and analyzed on a Varian 3700 gas chromatograph with autosampler and electron capture detector. A Hewlett-Packard 5880 controller/integrator was used to control the Varian gas chromatograph.

Aerobic composting resulted in the greatest decrease in PCB concentration, with an average reduction of 62 percent in four weeks. Residual concentrations ranged from 504 to 688 ppm. Anaerobic composting resulted in 27 to 47 percent reduction in four weeks, with residual concentrations ranging from 825 to 1,120 ppm.

The results of composting will, of course, depend upon the kind of microorganisms present. This study evaluated the effect of composting of individual isomers by comparing selected normalized areas of the chromatograms with those of controls. These comparisons showed significant decreases in the trichlorobiphenyls and one of the tetrachlorobiphenyls contained in the Aroclor 1242 after two weeks. No decrease in the higher chlorinated biphenyls was observed for this period. After 4 weeks, however, significant decreases in all of the chlorinated biphenyls occurred, with a loss of 25 percent of the trichlorinated biphenyls remaining. Anaerobic composting showed significant decreases in all of the chlorinated biphenyls also after 4 weeks.

Composting would appear to require considerable work-site space to handle the sludge, with considerable monitoring to determine the progress of the process. Lack of control of weather and other conditions would make the process uncertain in terms of time and effort required.

5.3.1.6.1 Cost--Data for composting are insufficient to provide a basis for cost estimates. Considerable extrapolation of the performance data would be required to project process conditions for desired residual PCB concentrations.

5.4 SUPPORTING PROCESSES

The dredging of submerged sediments is a necessary step prior to application of the treatment processes, except, perhaps, for the Sybron process. Many of the treatment processes have wastewater streams, the cleanup of which must be considered in their application. This section assesses dredging and wastewater treatment as supporting processes.

5.4.1 Dredging

5.4.1.1 Classes of Dredges--

Dredging practices have historically been designed to achieve the greatest possible economic return, with secondary consideration of environmental aspects. Because sediment removal is required as a first step in the application of most treatment technologies, the various approaches to dredging have been evaluated for suitability in bottom recovery of hazardous chemicals (Hand and Ford 1978). For the evaluation, dredging equipment has been classified according to mode of operation: mechanical, hydraulic, pneumatic, and special purpose (other). It is recognized that these classes are neither mutually exclusive nor parallel. However, they do serve to sort the equipment conveniently for comparison of suitability for various job sizes and sediment properties and for assessing their overall potential use in different scenarios, e.g., nonnavigable waters and navigable rivers.

Mechanical dredges remove bottom sediments by directly applying mechanical force to dislodge, excavate, and bring to the surface material at almost in situ densities. Most mechanical dredges deposit the dredged material into scows or barges for transport to a disposal site. Two basic configurations useful in dredging hazardous materials or contaminated sediments are the clamshell or grab dredge and the dipper dredge. Both types are normally barge-mounted and deposit excavated material into scows or a disposal area immediately adjacent to the worksite. Production rates vary according to cycle time and bucket capacity up to a maximum of about 380 m^3/h (500 yd^3/h), limiting them to spills covering relatively small areas.

Mechanical dredges cause turbidity and resuspension of sediment due to loss of fines during the hoisting process. They would be ineffective against a free liquid contaminant on the bottom. Mechanical dredges can work in relatively close quarters and around structures, obstacles, and debris. The clamshell is capable of deep water excavation in excess of 30.5 m (100 ft).

Hydraulic dredges, including plain suction, dustpan, cutterhead, and hopper dredges, remove and transport sediments in liquid slurry form using diesel- or electric-powered hydraulic pumps with discharge pipes ranging from 15 to 122 cm in diameter. The slurries, containing 10 to 20 percent solids by weight, are normally transported through pontoon-supported pipelines for distances up to several thousand meters. The hopper dredge stores the material onboard instead of transporting it.

The plain suction dredge entrains a water-sediment mixture and is limited to free-flowing sediments such as sand or unconsolidated silts and clays. It would probably be effective against intact masses of liquid or granular solid chemicals.

The dustpan dredge uses high-pressure water jets around the edges of the flared dredging head to loosen cohesive sediments and create a slurry. This action often causes relatively high turbidity in the dredging area.

The cutterhead dredge employs a powerful rotating mechanical digging apparatus to loosen hard materials and generate the slurry.

Hydraulic pipeline dredges are capable of very high production rates, e.g., in excess of 7,650 m^3/h (10,000 yd^3/h) for the largest diameter pipelines. They are cumbersome, however, because they rely on anchors, cables, and winches to move them across the worksite.

Hopper dredges are large, self-propelled, seagoing vessels with on-board storage hoppers ranging in capacity from 382 to over 6,100 m^3. They have suction pipes mounted on hinged drag arms on each side of the vessel hull. The drag arms trail back as the dredging head is dragged along the bottom at forward speeds up to approximately 13.3 km/h. During normal operation, the heavier sediments settle in the hopper, and excess water with considerable suspended fine-grained matter flows over weirs into the water, a practice that would generally not be acceptable when dredging hazardous material. These dredges can work in relatively rough and open water, in relatively high currents, and in bad weather. They can also work in shipping lanes with little disruption of traffic.

The pneumatic dredge features a crane-suspended pneumatic pump, but otherwise it is basically a hydraulic pipeline system. The pneumatic pump is operated by an air compressor aboard the barge. The pump consists of three cylinders that are alternately filled with sediment by hydrostatic pressure and emptied through check valves into a common header line by closing the inlet and applying compressed air. The sediment does not have to be in liquid slurry form; rather, it can be handled with solids contents corresponding to a plastic state or up to about 70 percent solids by volume. There is no theoretical depth limitation to pneumatic pumps as there is with surface-mounted centrifugal pumps; moreover, because they are crane-mounted, pneumatic systems could be useful in and around port structures. The normal mode of operation is with a scooplike dredging head that is pulled with cables into the excavation, resulting in a minimal solids resuspension.

A pneumatic dredge was used in the Duwamish PCB incident as well as several harbor cleanup operations in Japan. The pneumatic dredge appears to have high potential in the cleanup role.

Special purpose dredges include small hydraulic dredges such as the MUDCAT, the handheld suction devices, and the land-based earth-loading equipment used in the dredging mode. The MUDCAT is available from the National Car Rental agency, its designer and developer. It has undergone limited EPA testing in a hazardous materials cleanup role. It is a 9-m, pontoon-mounted, 20-cm hydraulic pipeline dredge featuring an augerlike cutting device mounted horizontally along a dozertype blade that feeds sediment to the suction intake of a diesel-driven centrifugal pump. The system is mounted on a hydraulic boom. The MUDCAT can dredge a swath 2.4 m wide by 0.46 m thick in waters as shallow as 0.46 m. Its maximum dredging depth is 4.6 m.

Handheld devices include a suction hose manipulated by a diver, with a pump and storage tank aboard a barge, boat, or land-based truck. Practical use would be limited to very small spills, precision dredging of intact masses of contaminant, or well-defined concentrations in difficult locations.

Land-based earth-loading equipment ranging from farm-tractor-sized loaders and backhoes to giant shovels and draglines used in strip mining could have valuable application to spill response, particularly for land spills and spills in small streams.

5.4.1.2 Dredge System Evaluation--

In a study of the impact of dredging, Carcich and Tofflemire (1981) examined potential adverse effects on the ecology and on the quality of drinking water drawn downstream from Hudson River sites of contamination. They concluded that ecological effects would not be significant and that dredging would reduce the overall risk of contamination of downriver water supplies.

The basic types of dredges have been evaluated by Hand and Ford for overall potential for hazardous material contaminated sediment recovery in different general environmental settings. Their ratings for nonnavigable waters and for rivers are shown in Tables 8 and 9. The column headings correspond to those site-specific factors identified as likely to be critical in each general setting and that are at the same time amenable to at least a qualitative numerical rating.

Each major type of dredge has been assigned a numerical score from 0 (worst) to 10 (best) for each of the rating criteria. Each of the criteria is assigned a weighting factor in accordance with its relative importance in influencing the suitability of dredges in each of the spill settings. A weighted average is computed to arrive at a score between 0 and 10 for each dredge in each spill setting; the weighted average score should be viewed as an overall indication but not an absolute measure of the dredge's potential for use in a given setting. Dredges with higher scores may typically do a better, faster, or more complete job with less harm to the environment, based on the criteria used, than those with lower scores. The particular circumstances present at an actual spill site would, of course, have to be examined and weighed against the capabilities of specific candidate dredges before a final decision could be made.

The "notes" columns in the tables are for certain qualifications, limitations, and other points that deserve special mention but are not reflected in the ratings themselves.

This evaluation makes no attempt to consider or quantify the possible influence of chemical-specific considerations. Dredging to remove hazardous chemicals from the bottom is principally a material relocation problem and the particular chemical spilled in most cases does not add significantly to the

TABLE 8. DREDGE EVALUATION MATRIX; SPILL SCENARIO: LAND AND NONNAVIGABLE WATERS--ALL SPILL SIZES

	Job size compatibility							Overall potential			
	Small <1,000 yd^3 (765m^3)	Medium 1,000-<200,000 yd^3 (153,000 m^3)	Large >200,000 yd^3 (>153,000 m^3)	Solids content	Resuspension of sediments and contaminants	Debris and structural obstacles	Transportation /mobilization time	Small yardage	Medium yardage	Large yardage	Notes
Weighting Factor	5	5	5	1	2	1	2	NA	NA	NA	NA
Mechanical	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Dipper			(Setting normally inaccessible to this type of equipment)								
Clamshell											
Hydraulic	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
Cutterhead (and plain suction)			(Setting normally inaccessible to this type of equipment)								
Dustpan											
Hopper											
Pneumatic	6	8	6	7	7	7	3	5.8	6.7	5.8	a,b,c
Other											
Mudcat	9	7	2	6	6	4	7	7.4	6.5	4.2	
Handheld vacuum	5	3	0	2	9	8	8	6.3	5.4	4.0	a,d
Land-based earth-loading equipment	9	9	9	10	2	8	9	7.7	7.7	7.7	e

[a] Plain suction will be effective only in free-flowing sediments such as sands; unconsolidated silty, clayey, or organic sediments; and liquids.

[b] Pneumatic systems that normally are operated in a plain suction mode could be operated with a variety of suction head devices such as augers and cutters.

[c] Equipment can be land-based and/or operated from the shore.

[d] Handheld vacuum will seldom be suitable as a first-line recovery device due to extremely limited production capacity. Probably will be most useful for precise cleanup and peripheral operations; in situations of small, concentrated well-defined spills; and for cleanup in close quarters.

[e] Includes such equipment as backhoes, front-end loaders, dozers, draglines, and shovels varying in size from small farm tractor mounted to large ship mining equipment.

NOTE: The numerical scores reflected in this table should not be contrued as an absolute measure of the dredge's value.

TABLE 9. DREDGE EVALUATION MATRIX; SPILL SCENARIO: RIVERS--ALL SPILL SIZES

	Job size compatibility											Overall potential			
	Small <1,000 yd^3 (765m^3)	Medium 1,000-200,000 yd^3 (153,000 m^3)	Large >200,000 yd^3 (>153,000 m^3)	Solids Solids content	Resuspension of sediments and contaminants	Dredging depth limitation	Vessel draft limitation	Debris and structural obstacles	Hindrenc to traffic	Current limitation	Transportation /mobilization time	Small yardage	Medium yardage	Large yardage	Notes
Weighting Factor	5	6	6	1	3	1	2	2	1	1	2	NA	NA	NA	NA
Mechanical															
Dipper	7	5	1	10	1	4	8	7	7	8	4	5.8	5.2	3.9	a,b,g
Clamshell	8	6	2	10	1	10	8	9	7	6	4	6.6	6.8	4.7	a,b,g
Hydraulic															
Cutterhead (and plain suction)	3	7	9	5	5	6	7	3	3	7	2	4.1	5.4	6.8	c,e,f
Dustpan	3	7	8	5	5	6	7	3	3	7	2	4.1	5.4	6.7	f
Hopper	3	7	7	5	5	6	2	1	9	9	4	4.0	5.3	5.3	f
Pneumatic	6	7	4	7	7	10	7	9	3	6	5	6.6	6.9	5.9	c,d,g
Other															
Mudcat	9	5	2	6	6	3	9	4	5	4	8	7.8	5.7	4.7	i
Handheld vacuum	5	1	8	2	9	6	10	10	6	1	9	6.8	5.6	5.3	c,h

[a] Can only be used for a solid contaminant unless suction will be effective only in free-flowing sediments such as sands; unconsolidated silty, clayey, or organic sediments; and liquids.

[b] Pure mechanical devices will be relatively ineffective on hard rock or hardpan clay sediments.

[c] Plain suction will be effective only in free-flowing sediments such as sands, unconsolidated silty, clayey, or organic sediments, and liquids.

[d] Pneumatic systems that are normally operated in a plain suction mode could be operated with a variety of suction head devices such as augers and cutters.

[e] Cutterheads should be turned off when operating in a rock or hardpan bottom to avoid unnecessary dispersion of contaminant and/or damage to dredging equipment.

[f] Dredging depths can be effectively increased with the addition of auxiliary booster pumps at the suction head.

[g] Equipment can be land-based and/or operated from the shore.

[h] Handheld vacuum will seldom be suitable as a first-line recovery device due to extremely limited production capacity. Probably will be most useful for precise cleanup and peripheral operations; in situations of small, concentrated, well-defined spills; and for cleanup in close quarters.

[i] Mudcat cannot be used in open water situations due to severe depth and wave height limitations but probably would be most effective in small, nonnavigable streams.

NOTE: The numerical scores reflected in this table should not be construed as an absolute measure of the dredge's value.

problem of assessing the suitability of a dredging technique. The same disadvantages are usually present (e.g., resuspension of the contaminant) regardless of the particular chemical. However, precautionary measures appropriate to the specific chemical being recovered should always be diligently observed. Also, the ratings do not take into account the problems of dredged material transport, treatment and disposal. These factors may sometimes be found to be controlling in selecting a system.

5.4.2 Wastewater Treatment Methods

5.4.2.1 Mechanical Removal--

The removal of PCB in primary sedimentation processes of sewage treatment has been found to vary between 50 and 75 percent (McIntyre, Perry, and Lester 1981). It would seem that, due to their nonpolar nature, the PCBs tend to adsorb onto suspended solids and partition into fats and lipid material present in the raw sewage. Sedimentation processes appear to concentrate the PCBs into the sludges produced.

5.4.2.2 Activated Sludge--

Activated sludge methods do not apply directly to the decontamination of PCB-contaminated sediments because their function is to remove contaminants from wastewaters. They may be useful, however, as adjunct treatments wherever a sediment treatment process generates a waste stream that is aqueous and contains dissolved PCBs. The processes have not been adapted to the immediate problem of PCB degradation in nonaqueous media.

Wastewaters are subjected to aerobic-activated sludge treatment in continuously fed tanks where microorganisms digest and flocculate the organic waste. The microorganisms (activated sludge) settle from the aerated liquor in a final clarifier and are returned to the aeration tank. The purified effluent is discharged from the final settling tank. Dissolved oxygen extracted from the liquor is replenished by air sparged into the aeration tank. The various engineering unit operations are sedimentation, aeration, clarification, sludge dewatering, and chemical storage.

Using a continuously fed activated sludge unit, with a feed rate of 1 mg/48 h, Tucker et al. (1975) obtained the following degradation of PCBs:

Aroclor 1221, 81 percent; Aroclor 1016, 33 percent; Aroclor 1242, 26 percent; Aroclor 1254, 15 percent. The lower chlorinated isomers were shown to be more readily degraded than the higher chlorinated isomers (Mihàshi 1975). Monochlorinated isomers were degraded 100 percent within 6 h; tetrachlorinated isomers were degraded only 42 percent in 15 d. The major microorganisms found in the activated sludge were alkaligenes odorans, alkigenes denitrificans, and an unidentified type of bacterium.

5.4.2.3 Trickling Filter--

Trickling filters use crushed rock, slag, or stone to provide a surface area for biological growth and passages for liquid and air. As the wastewater flows over the microbial surface, the soluble organic material is metabolized and the insoluble material is adsorbed onto the media surface. Biological components of the filter may include bacteria, fungi, and protozoa. Nitrogen-fixing bacteria are contained at the bottom of the filter.

A trickling filter consists of a rotary distributor, an underdraw system, and the filter media. Because an aqueous flow medium is necessary, only dilute soluble PCB isomers may readily be contacted with the active microbes. No data were found relating specifically to the PCB-destruction performance of trickling filters.

5.4.2.4 Special Biological Treatment Processes--

Several newer biological systems for the treatment of wastewaters are emerging, none of which has been demonstrated for PCBs. These include the Biodisc, a type of thin-film biodegradation system in which large plastic discs are partially submerged in the aqueous waste solution. Aerobic microorganisms colonize the disc surfaces and are oxygenated as the discs rotate. This system creates a well-aerated surface requiring little space.

The Bio-Surf^{TM} process creates anaerobic conditions by enclosing a submerged Bio-Surf system and adding a carbon source such as methanol.

Ecolotrol, Inc., has developed a full-scale biological fluidized-bed process, utilizing sand as the particle growth medium. A large population of microorganisms is generated, which makes possible a faster than conventional treatment. A clarifier is not required (Wilkinson et al. 1978).

A freeze-dried biochemical solution containing a mutant bacteria and various substances to facilitate their growth has been shown by Wormes Biochemicals to degrade various chlorinated hydrocarbons (Phenobac^{TM} 1977).

5.4.2.5 UV/Ozonation--

PCB-contaminated wastewaters have been treated by ultraviolet radiation combined with sparged ozone (Arisman and Musich 1981). In bench- scale tests, the water was passed through a multistage reactor equipped with up to 30- to 40-watt low-pressure UV lamps. Ozone, generated from liquid oxygen, was diffused into each stage. The treated effluents showed 91 to 100 percent destruction of PCBs.

5.4.2.6 Carbon Adsorption--

Adsorption is useful for removing chlorinated hydrocarbons from aqueous waste streams. The stream is contacted with activated carbon by passing it through a vessel filled with a carbon slurry or with carbon granules. Impurities from the aqueous streams are removed by adsorption onto the carbon surface. The complete adsorption system usually consists of a few columns used as contactors connected to a regeneration system. After a certain period of time, the carbon adsorptive capability is exceeded, and the carbon must be regenerated or replaced by fresh carbon, which is also periodically added to the system to replace that lost during regeneration and transport. Activated carbon has an affinity for organics, and its use for organic contaminant removal from wastewater is common. Carbon adsorption is particularly favorable when the solutes have a high molecular weight and low water solubility, as is the case with dissolved PCBs. Carbon adsorption is one of the most promising water treatment systems for removing dissolved PCBs, as indicated in a study done by Versar, Inc., in 1976. It was found in that study that the activated carbon system was capable of reducing the concentration of PCBs in the aqueous effluent to less than 1 ppb.

In 1976, the General Electric Capacitor Products Department installed a system to eliminate the discharge of PCBs to the Hudson River from the Hudson Falls and Fort Edward manufacturing sites. All wastewater discharged from the site was treated by carbon adsorption before the discharge to the river. This adsorption process worked extremely well for dilute aqueous streams contaminated with PCBs. It was found that, while the carbon treatment system could reduce the concentration of PCBs in the aqueous effluent to less than 1 ppb, it was not a very cost-effective method. This, coupled with carbon disposal or regeneration requirements, provided a basis for the EPA and the General Electric Capacitor Products Department to investigate alternate treatment systems, i.e., UV-ozonation and catalytic reduction (Arisman 1981).

Results of adsorption treatment of water polluted with PCB (Aroclor 1260) have also been reported by Gilmer and Freestone (1978). Using sand filtration and carbon adsorption, PCB concentrations of approximately 19 g/mL were reduced to less than 0.05 to 0.2 g/mL. The authors also used the Mobile Physical-Chemical Treatment System (EPA Edison) to treat impounded water containing 85 g/mL of PCB. Using bag filters and carbon adsorption, the concentration was reduced to 4.5 g/mL after the bag filters and to <0.2 g/mL after carbon adsorption. The overall treatment effectiveness amounted to 99 percent removal.

SECTION 6

CHARACTERIZATION AND RANKING OF ALTERNATIVE TREATMENT PROCESSES

This section provides two comparisons of the alternative treatment processes assessed in Section 5: characterization and ranking. The characterization provides for objective comparison of the processes. The ranking provides a subjective comparison of the processes based on the seven criteria described in Section 4.

6.1 CHARACTERIZATION

Table 10 summarizes five characteristics of the processes: unit operations, available capacity, conditions/limitations, concentration handled, and any generated RCRA wastes. The unit operations employed are given, and each is identified by a number. Generally, a greater number of unit operations will mean a greater effect on treatment costs.

None of the processes has currently available capacity approaching that required for major cleanups. Therefore, the time required to build capacity is listed. Construction time ranges from 12 to 24 months.

Certain conditions that typify the process or limit its versatility are given in column 4 of Table 10. More details of the operations are given in Section 5.

The data from studies of the processes were examined for ranges of PCB concentrations handled to date. Generally, the values are not limitations on the process, but only on the data acquired. The value $\leq$300 ppm for the Bio-Clean process may, however, be a limitation requiring process adjustment to control.

TABLE 10. TREATMENT PROCESS ASSESSMENT

Process	Unit operations	Available capacity (or time to provide)	Conditions and limits	Concentration handled	RCRA waste generated
Chemical					
Supercritical water oxidation	1,4,10	—	20-40% solids; 374 °C, 23.3 MPa organic content >5% or supplemental fuel	>3000 ppm	None
KPEG, Terraclean-CL	1,3,4,7	(24 mo)	150 °C, 0.5-2 h	500 ppm or greater	w.w.tr. act. carbon
KPEG, NYU	1,2,3,4,5, 6,7,9	—	—	—	—
KPEG, EPA in-house[b]	Fundamental studies				
LARC	1,2,5,15,	(24 mo)	tolerates 25% water.	480 ppm	None
Advanced electric reactor (J. M. Huber)	7,8,12,13 14	(16 mo)	2204 °C, 2,400 kWh/m^3 needs predryer	>3000 ppm	None
Physical					
O. H. Materials methanol extraction	2,7,8,14 15	—	predry to <1% moisture	>400 ppm	PCB-loaded carbon from solvent cleanup
"Soilex" kerosene/water	1,2,5,15	—	25% of kerosene solvent retained in soil; 3 d per batch	to 350 ppm tested	Concentrated PCB from still to incineration
Acurex solvent wash	2,4,5,6, 10,11	—	3-12 washes, tolerates <40% water.	up to 1,983 ppm	Concentrated PCB's to KPEG
Vitrification	8,12,14	—	Electrical power usage increases with soil moisture; submerged sediments dredged and treated	500 ppm	None

(continued)

TABLE 10 (continued)

Process	Unit operations	Available capacity (or time to provide)	Conditions and limits	Concentration handled	RCRA waste generated
Biological					
Composting	15,16	(16 mo)	Seasonal effects, reaction time must be >4 weeks	1,590 ppm	Treated material is still a RCRA waste
Bio-Clean	1,2,17	27 m^3/d available, 12 mo for full-size	Proved for PCP, laboratory confirmed for PCB's	≤300 ppm	None
Sybron Bi-Chem 1006	15,17	—	Unknown	Unknown	Unknown

NOTE—Unit operations key:

1. Liquid/solids separation
2. Extraction/solubilization (liquid-solids)
3. Liquid/liquid extraction
4. Chemical reactor
5. Stripping still
6. Solvent recovery still
7. Adsorption
8. Dryer (solids)
9. Dryer (liquids)
10. Filtration
11. Steam cleaning
12. Thermal reactor
13. Grinding
14. Air pollution controls
15. Landfarm
16. Innoculation/digestion
17. UV light reactor

Table 10 also identifies any RCRA waste streams generated by the process. Possible treatments of some of these are discussed in Section 5.

Table 11 lists five additional characteristics of the processes and the rating developed in the ranking process. The characteristics shown here relate to the needs for further process development, listing, and evaluation. The listing begins with an indication of the process status in terms of stages of development completed. The processes range in stages completed from concept to pilot plant.

Both PCB destruction and residual PCB concentration in treated sediments are given to the extent available. Certain processes may require extension of the unit operations (e.g., more stages of extraction) to attain the required performance levels.

Test and evaluation data needs are indicated for each process. Needs vary from none (AER process) to complete site-specific evaluation.

The estimated costs of applying the process are listed in $\$/m^3$. These are displayed in Figure 16. Landfill costs and incineration costs are also shown. Although cost estimates lack the necessary accuracy at this stage of development of the alternative processes to serve as the sole criterion of potential, they nevertheless indicate that seven of the processes may cost no more than landfill and five could cost less. (Cost estimates were not made for the Sybron process and composting.)

6.2 RANKING OF TREATMENT PROCESSES

In contrast to process characterization, ranking is subjective. An attempt was made to define and determine a single number that could represent the overall position of each process relative to an arbitrarily defined perfect process. To do so, factors considered were given ratings as described below.

TABLE 11. TREATMENT PROCESS ASSESSMENT

Process	Status[a]	Estimated D/D/R efficiency, %[b]	Estimated residual PCB, ppm	Test and evaluation data needs	Estimated costs, $/m^3	Rating[c]
Chemical/physical						
Supercritical water oxidation, Modar	Field test with PCB liquids	>99.9995	<0.1 ppb	1,2,3,4,5,6,7,	250-733	4.58
KPEG Terraclean-CL	Pilot tests	>98	<1 ppm	1,6	208-375	5.42
LARC	Lab tests	>90	38-50	2,3,4,5,6,7	223-336	5.26
Advanced electric reactor	Pilot tests	>99.9999	<1 ppb	None[d]	830-943	4.58
Physical						
O. H. Materials, methanol extraction	Field tests under way	97	<25 ppm	2,3,6,7	401-514	4.16
Soilex	Pilot tests	95 (3 stages)	6-9 ppm	5,6,7	856-913	3.26
Acurex solvent wash	Pilot-scale (field tests planned)	e	<2 ppm	Identity of mixed solvent, 6,7	196-569	5.21
In-situ vitrification Battelle Pacific NW for EPRI	Pilot test of soil	99.9	None in vitrified block, 0.7 ppm in adjacent soil	6	255-548	4.53

See footnotes at end of table.

(continued)

TABLE 5 (continued)

Process	Status[a]	Estimated D/D/R efficiency, %[b]	Estimated residual PCB, ppm	Test and evaluation data needs	Estimated costs, $\$/m^3$	Rating[c]
Biological						
Composting, aerobic	Lab-scale	62	504-908	4,5,6	—	2.47
anaerobic	Lab-scale	18-47	825-1268	4,5,6	—	2.47
Bio-Clean, aerobic	Bench-scale	99.99	25 ppb	3,5,6,7	191-370	4.84
Sybron Bi-Chem 1006	Lab-scale and concept	50	—	3,4,5,6,7	—	1.48

NOTE—Data needs key:

1. D/D/R data
2. Residual PCB data
3. Unit operations data
4. Bench-scale data
5. Pilot-scale data
6. Field test data
7. Cost data
8. RCRA waste

[a] Status is defined in terms of the types of studies completed.

[b] D/D/R = destruction/detoxification/removal.

[c] The rating was obtained as shown by the example, under Characterization.

[d] AER is fully permitted under TSCA in EPA Region IV for destruction of PCB.

[e] Treatment is continued until a residual of <2 ppm PCB's is obtained.

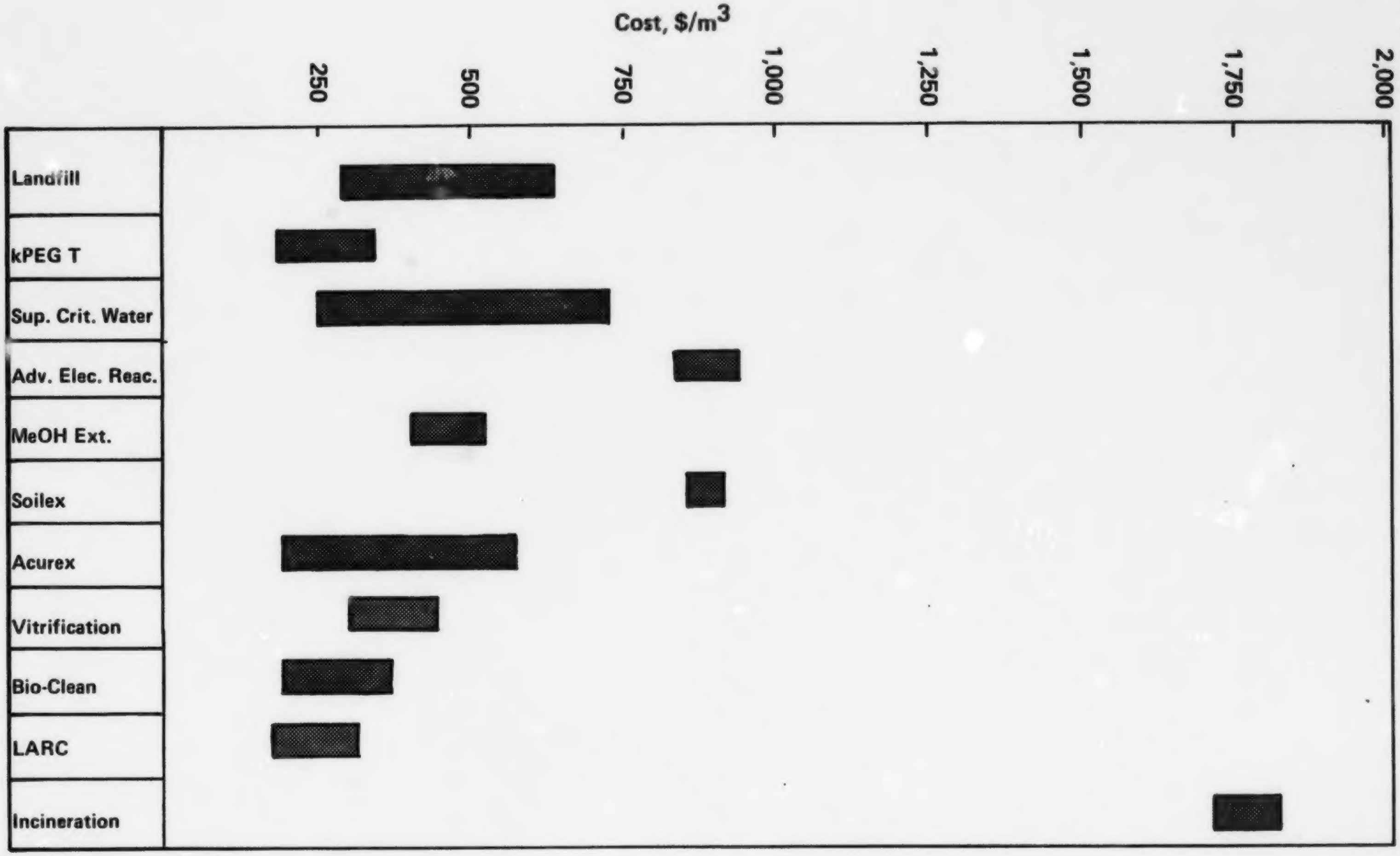


Figure 16. Alternative treatment costs, PCB D/D/R processes.

6.2.1 Residual PCB Concentration in Treated Sediments

The goal set for process performance is to reduce the PCB concentration in treated sediments to background levels of 1 to 5 ppm. Several of the processes were found to meet this goal. Those that showed reduction to less than 2 ppm were assigned a rating of "6". Those that attained a level between 2 and 10 ppm were assigned a "4". Those with residual concentrations greater than 10 ppm were rated "2".

6.2.2 Available Capacity

Available capacity was found not to exist for any of the processes. However, several were developed sufficiently to permit projections of the time required to build a facility for application of the treatment. Those for which such projections could not be made were rated "2". Those requiring 24 or more months were rated "4". Those requiring 12 to 16 months were rated "6".

6.2.3 Conditions/Limitations

Conditions/limitations that were rated were tolerance for water, required processing time, and controllability of process conditions. Those treatments that could tolerate water up to about 40 percent would not require a drying step with its attendant fines control problems. Those requiring only 1 day for treatment could generally show a faster rate of cleanup than those requiring 3 days. Some biological processes required more than 3 weeks. The treatments generally provided control of the processing conditions; however, a few (e.g., composting) would not necessarily do so. The three conditions/limitations were ranked as follows:

Conditions/limitations	Rank
Tolerates to 40 percent water and treats in 1 day	6
Sediment needs to be dried	5
Tolerates to 40 percent water and treats in 3 days	4
Tolerates water and treats in >3 weeks	3
Sediment needs to be dried, treats in >3 weeks	2
Processing conditions uncontrollable	1

6.2.4 Concentration Range Handled

Concentration range handled in data developed for the processes ranged from unknown to 3,000 ppm. Ratings were assigned based on the upper limit of feed concentration. The ratings were as follows:

PCB concentration treated, ppm	Rank
>3,000	6
2,000 to 3,000	5
1,500 to 2,000	4
500	3
250 to 350	2
Unknown	1

6.2.5 Status of Development

Status of development ratings were "1" for no data, "2" for laboratory-scale tests completed, "3" for bench-scale tests completed, "4" for pilot-scale tests completed, "5" for field tests completed; and "6" for commercial system designed and ready for construction.

6.2.6 Test and Evaluation Data Needs

Test and evaluation data needs could be rated differently, depending upon the purpose. For indicating the extent to which a treatment process is readied for use, the more data that are available the better. For indicating the need to support a very promising technology that lacks sufficient progress, the potential and the data needs should be rated in combination. The ratings used here are for the former purpose and are as follows:

Test and evaluation data needs	Rank
None except permits and checkout	6
Field tests	5
Pilot tests and costs	4
Laboratory and bench tests	3
Conceptual treatment process design	2
D/D/R data, residual PCB data, RCRA waste data	1

6.2.7 Estimated Costs

Estimated costs were assembled graphically (Figure 16). The estimates were then rated by comparing the range of the cost estimates obtained with the cost of placing them into a chemical waste landfill. Treatment processes showing the lowest estimated cost range were rated "6"; those showing a probable cost lower than landfill were rated "4"; those showing an estimated cost equal to landfill were rated "2"; and those showing an estimated cost range greater than landfill were rated "1".

6.2.8 Overall Ranking

Overall ranking was accomplished through the use of weighting factors assigned to each rated factor. The weighted average rank was then obtained by summing the products of the weighting factors and the ratings and dividing by the sum of the weighting factors. The weighting factors were:

Factor	Weight
Residual PCB concentration	5
Capacity	2
Conditions/limitations	3
Concentration range handled	2
Status of development	2
Test and evaluation data needs	1
Estimated costs	4

The weightings tend to give greatest emphasis to the ability of the treatment to reduce the PCBs and to the probable cost of the treatment. Much less emphasis is placed on the status of development. Thus, an almost fully developed process with an extremely high cost would be ranked lower by application of the weighting process than a less developed process with a much lower potential cost. Test and evaluation data needs have not been heavily weighted because nearly all the alternative treatment processes that show low potential cost require more data to be proven.

The perfect process for treating PCB-decontaminated sediments would show the following levels for each ranking factor and would receive, using the ratings given, a weighted rating of 6.0:

Factor level	Rating, R	Wt	R x Wt
1. Residual PCB, treated sediment less than 1 ppm	6	5	30
2. Capacity adequate for site cleanup available in 12-16 mo.	6	2	12
3. Tolerates to 40 percent water and treats in 1 day (24 hr)	6	3	18
4. Handles concentrations greater than 3,000 ppm	6	2	12
5. Commercial system designed and ready for construction	6	2	12
6. No test and evaluation data needs except permits and checkout	6	1	6
7. Lowest estimate cost range among alternative emerging technologies	6	4	24
Total R x Wt $\sum$ R x Wt			114
Weighted rating ($\sum$ R x Wt)/$\sum$Wt			6

The weights were assigned subjectively to emphasize low residual PCB, then estimated cost and water tolerance. The weights were used as multipliers to give the chosen emphasis.

This procedure established a range of 1.48 to 6.0 for the weighted rating. Under this procedure, one process just emerging, without a fully developed concept of its operations and with very limited data available for evaluation, received a weighted rating of 1.48. The further developed processes received ratings up to 5.42 (Table 12). The difference (6 to 5.42) is a subjective indication that further research would be productive in regard to all these criteria considered collectively. Scores assigned for each factor are also listed in Table 12. The weighted ratings show two ties at 4.58: Supercritical Water, and the Advanced Electric Reactor.

Based on the weighted ratings, the processes rank as follows from highest to lowest: KPEG, LARC, Acurex, Bio-Clean, Modar-Supercritical Water, Advanced Electric Reactor, Vitrification, OHM Extraction, Soilex, Composting, and Sybron Bi-Chem 1006 PB/Hudson River Isolates.

TABLE 12. RANKING OF EMERGING TREATMENTS FOR PCB-CONTAMINATED SEDIMENTS

	Factor relative weight	Supercritical water, Modar	KPEG Terraclean	Advanced electric reactor	O. H. Materials extraction	Soilex	Acurex	Vitrification	Composting	Bio-Clean	Sybron Bi-Chem 1006	LARC
Residual PCB	5	6	6	6	6	4	6	6	2	6	2	6
Available capacity	2	2	4	6	6	2	2	4	2	6	2	4
Conditions limitations	3	6	6	5	5	4	6	5	1	4	1	6
Concentration range handled	2	6	5	6	5	5	5	6	3	2	1	5
Status of development	2	3	4	4	4	4	4	4	2	3	2	3
Test and evaluation data needs	1	1	5	6	4	4	5	5	3	4	1	4
Estimated costs	4	4	6	1	2	1	6	2	1	6	1	6
Weighted rating		4.58	5.42	4.58	4.16	3.26	5.21	4.53	2.47	4.84	1.48	5.26

SECTION 7

BIBLIOGRAPHY

Adams, G.P., and R.L. Peterson. 1985. Non-Sodium Process for Removal of PCBs from Contaminated Transformer Oil, PCB Seminar, EPRI, Seattle, Washington, October 22-25.

Addis, G., and J. Marks, eds. 1982. Proceedings: 1981 PCB Seminar, Dallas, Texas, December 1-3, 1981. EPRI EL-2572, Electric Power Research Institute, Palo Alto, California. 331 pp.

Agnew, R.W. 1984. Removal and Treatment of Contaminated River Bottom Muds: Field Demonstration. NTIS Publication No. PB84-129022, EPA-600/52-84-006, U.S. Environmental Protection Agency, Cincinnati, Ohio. 70 pp.

American Petroleum Institute. 1983. Land Treatment--Safe and Efficient Disposal of Petroleum Waste. Washington, D.C., 21 pp.

Angiola, A.J., and J.M. Soden. 1982. Predicting and Controlling Downwind Concentrations of PCB from Surface Impoundments. In: Proceedings of the Annual Meeting of the Air Pollution Control Association. 75(4):82.

Arisman, R.K., R.C. Musick, J.D. Zeff, and T.C. Crase. 1981. Experience in Operation of a Ultraviolet-Ozone (Ultrox®) Pilot Plant for Destroying Polychlorinated Biphenyls in Industrial Waste Influent. In: Proceedings of the 35th Industrial Waste Conference, Purdue University, West Lafayette, Indiana, May 11-13, Ann Arbor Science, Ann Arbor, Michigan. pp. 802-808.

Bailin, L.J., and B.L. Hertzler. 1977. Development of Microwave Plasma Detoxification Process for Hazardous Wastes--Phase I. NTIS PB-268526, EPA-600/2-77-030, U.S. Environmental Protection Agency, Cincinnati, Ohio. 82 pp.

Bailin, L.J., and B.L. Hertzler. 1978. Development of Microwave Plasma Detoxification Process for Hazardous Wastes-Part I. Environ. Sci. Technol. 12(6):673-679.

Bailin, L.J., B.L. Hertzler, and D.A. Oberacker. 1978. Detoxification of Pesticides and Hazardous Waste by the Microwave Plasma Process. ACS Symposium Series, No. 73, American Chemical Society, Washington, DC, p. 49.

Baillod, R., et al. 1978. "Wet Oxidation of Toxic Organic Substances," presented at the Purdue Industrial Waste Conference, W. Lafayette, Indiana.

Ball, J., F. Prizmar, and P. Peterman. 1978. Investigation of Chlorinated and Nonchlorinated Compounds in the Lower Fox River Watershed. NTIS PB-292-818/2, EPA-905/3-78-004, U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, Illinois. 235 pp.

Bartos, M.J. 1978. NYC's Plan to Meet the Water Quality Challenge. Civ. Eng. (Am. Soc. Civ. Eng.) 48(11):80-84.

Bedard, D.L., et al. 1985. Rapid Screening Assay for PCB-Degradative Ability, Bio. Sci. Br., General Electric Company, Corporate Research and Development, Schenectady, New York 12301.

Berg, O.W., P.L. Diosady, and G.A.V. Rees. 1972. PCB Contamination of the Aquatic Environment in Ontario. Paper presented before the Division of Water, Air, and Waste Chemistry at the 173rd Meeting of the American Chemical Society, August 28-September 1, 12(2):59.

Bergh, A.K., and R.S. Peoples. 1977. Distribution of Polychlorinated Biphenyls in a Municipal Wastewater Treatment Plant and Environs. Sci. Total Environ. 8(3):197-204.

Billings, W.N., T.F. Bidleman, and W.B. Vernberg. 1978. Movement of PCB from a Contaminated Reservoir into a Drinking Water Supply. Bull. Environ. Contam. Toxicol. 19(2):215-222.

Boyd, J.W., 1985. Thermal Treatment of PCB's and PCB-contaminated Soils, EPRI. PCB Seminar Oct. 21-25, Seattle, Washington.

Brown, J.F., M.E. Lynch, J.C. Carnahan, and J. Singleton. 1981. Chemical Destruction of PCB's in Transformer Oil. Preprint Extended Abstract. Presented before the Division of Environmental Chemistry at the 182nd Meeting of the American Chemical Society, New York, New York, August 23-28, 21(2):90-92.

Brown, M.P. 1985a. Characterization of Hudson River Sediment Provided to American Toxics Disposal, Inc. by the New York State Department of Environmental Conservation. Office of Special Projects New York State Department of Environmental Conservation, Albany, New York. 7 pp.

Brown, M.P. 1985b. Letter to C.J. Rogers, May 24.

Brown, M. P. 1986. Letter of April 16 to Donald L. Wilson.

Brunelle, D.J., and D.A. Singleton. 1985. Chemical Reaction of Polychlorinated Biphenyls on Soils with Poly(Ethylene Glycol)/KOH. Chemosphere 14(2):173-181.

Bumpus, J.A., et al. 1985. Oxidation of Persistent Environmental Pollutants by a White Rat Fungus, Science 228, 1434-1436, June 20, 1985.

Business Week. 1978. The Lagging Cleanup of Great Lakes Pollution. Bus. Wk., May 29, p. 76.

Caplan, J. 1986. Personal Communication, February 6.

Carcich, I.G., and J. Tofflemire. 1983. PCB Cleanup Activities on the Upper Hudson River. In: Management of Bottom Sediments Containing Toxic Substances: Proceedings of the 7th U.S./Japanese Experts Meeting, National Technical Information Service, Springfield, Virginia, pp. 168-180.

Carcich, I.G., and T.J. Tofflemire. 1982. Disbribution and Concentration of PCB in the Hudson River and Associated Management Problems. Environ. Intl. 7(2):73-85.

Caron, R. 1985. Superfund Cleanup of PCB Contaminated Soil, Minden, West Virginia. Personal Communication, December.

Catelani, D., C. Sorlini, and V. Treccani. 1971. The metabolism of biphenyl by Pseudomaas Putida. Experimentia 27:1173-1174.

Centofanti, L.F. 1984. Analysis of PCB Chemical Destruction Effluents. Preprint Extended Abstract. Presented before the Division of Environmental Chemistry at the 185th Meeting of the American Chemical Society, St. Louis, Missouri, April 8-13, 24(1):11-12.

Chang, V.S., and D.A. Fast. 1983. PCBs Spill at Federal Pioneer Limited's Regina Plant. In: Proceedings of the Environment Canada 1st Technical Chemical Spills Seminar, Toronto, Canada, October 25-27, p. 225.

Chen, K. 1982. The Reclamation of Transformer Oils Containing PCBs by the Sunohio PCBX Process, Final Report. Prepared for the Tennessee Valley Authority Office of Power, Division of Energy Demonstrations and Technology, Chattanooga, Tennessee. TVA/OP/EDT-83/3, DE83 901683. 112 pp.

Childs, K. 1982. PCB Treatment and Destruction Technologies. In: Proceedings of the 28th Ontario Industrial Waste Conference, Ottawa, Ontario, Canada, June 13-16, Ontario Ministry of the Environment, Ontario, Canada. pp. 121-148.

Chu, N.S., and S.C Vick. 1985. Chemical Destruction of PCBs, EPRI PCB Seminar. Seattle, Washington. October 27.

Clark, R.R., E.S.K. Chian, and R.A. Griffin. 1979. Degradation of Polychlorinated Biphenyls by Mixed Microbial Cultures. Appl. Environ. Microbiol. 37(4):680-685.

Counsel, G. 1982. Wrench-Lok®: Grounding Connections Simplified. Paper presented before the Electrical Equipment Committee at the Pennsylvania Electric Association Fall Conference, Lancaster, Pennsylvania, September 14.

Craddock, J.H. 1982. Polychlorinated Biphenyls (PCBs) Disposal and Treatment Technologies: An Update. Paper presented at the Fertilizer Institute Environmental Symposium, San Antonio, Texas, March 8-10, p. 161.

Craft, T.F., R.D. Kimbrough, and C.T. Brown. 1975. Radiation Treatment of High Strength Chlorinated Hydrocarbon Wastes. NTIS PB-244388, EPA-660/2-75-017, U.S. Environmental Protecton Agency, Athens, Georgia, 33 pp.

Dallaire, G. 1979. Toxics in the N.J. Environment: Microcosm of U.S. Ills. Civ. Eng. (Am. Soc. Civ. Eng.) 49(9):74-80.

Dawes, I.W., and I.W. Sutherland. 1976. Microbial Physiology. John Wiley and Son, New York.

Dev, H., J.E. Bridges, G.C. Stesty, and C.J. Rogers. 1985. In-Situ Decontamination of Spills and Landfills by Radio Frequency Heating. Paper presented at the American Chemical Society National Meeting, Chicago, Illinois, September.

Edwards, B.H., J.N. Paullin, and K. Coghlan-Jordan. 1982. Emerging Technologies for the Control of Hazardous Wastes. EPA-600/2-82-011, NTIS PB 82-236993, U.S. Environmental Protection Agency, Cincinnati, Ohio. 145 pp.

Electrical World. 1978. One Solution to the PCB-Disposal Dilemma. Elect. World 190(9):52-53.

Environment Canada. 1983. Destruction Technologies for Polychlorinated Biphenyls (PCBs). Economic and Technical Review Report EPS 3-EC-83-1, Environmental Protection Service, Ottawa, Ontario, July (reprint). 81 pp.

Environment Canada. 1983. Proceedings of the Technical Seminar on Chemical Spills. Toronto, Canada, October 25-27, 291 pp.

Erler, T.J., J. Dragun, and D.R. Weider. 1983. Two Case Studies of Cost-Effective Remedial Actions for PCB Contaminated Soils. In: Proceedings of the 38th Industrial Waste Conference, Purdue University, West Lafayette, Indiana, May 11-13, Ann Arbor Science, Ann Arbor, Michigan, pp. 369-375.

Exner, J.H., ed. 1982. Detoxification of Hazardous Waste. Ann Arbor Science Publishers, Ann Arbor, Michigan. 362 pp.

Fedorko, J.W. 1982. Protection of the Hosensak 230 kV and Three Mile Island 500 kV Capacitor Banks. Paper presented at the Pennsylvania Electric Association Fall Conference, Lancaster, Pennsylvania, September 14.

FMC Corporation. (n.d.) Industrial Waste Treatment with Hydrogen Peroxide, Industrial Chemical Group, 2000 Market Street, Philadelphia, Pennsylvania.

Fox, L. L., and N.J. Merrick. 1983. Managing Polychlorinated Biphenyls in the Industrial Environment--A Case History. In: Toxic and Hazardous Waste: Proceedings of the 15th Mid-Atlantic Industrial Waste Conference, Lewisburg, Pennsylvania, June 26-28, Butterworth Publishers, Boston, Massachusetts, pp. 336-344.

Fradkin, L., and S. Barisas. 1982. Waste Management Options for PCBs. In: Industrial Waste: Proceedings of the 14th Mid-Atlantic Industrial Waste Conference, College Park, Maryland, June 27-29, Ann Arbor Science, Ann Arbor, Michigan, pp. 398-407.

Furakawa, K. 1982. Microbial degradation of PCBs, pp. 33-57. A.M. Chakrabarty (Ed.), Biodegradation and Detoxification of Environmental Pollutants, CRC Press, Inc. Boca Raton, Florida.

Ghassemi, M., and M. Haro. 1985. Hazardous Waste Surface Impoundment Technology, J. Envir. Eng 111, 5, October.

Gilmer, H., and F.J. Freestone. 1978. Cleanup of an Oil and Mixed Chemical Spill at Dittmer, Missouri, April-May 1977. In: Proceedings of the 1978 National Conference on Control of Hazardous Material Spills, Miami Beach, Florida, April 11-13, Information Transfer, Rockville, Maryland, pp. 131-134.

Githens, G.D. 1984. Carbon Adsorption Onsite for Remedial Actions. Pollut. Eng. 16(1):22-25.

Gruenfeld, M., F. Freestone, and I. Wilder. 1978. EPA's Mobile Lab and Treatment System Responds to Hazardous Spills. Ind. Water Eng. 15(5):19-23.

Hancher, C.W., J.M. Napier, and F.E. Kosinski. 1984. Removal of PCB from Oils and Soils. Preprint prepared for submission to: 5th Department of Energy Environmental Protection Conference, November 6-8, Albuquerque, New Mexico, DE85 002619. 7 pp.

Hand, T.D., and A.W. Ford. 1978. The Feasibility of Dredging for Bottom Recovery of Spills of Dense, Hazardous Chemicals. In: Proceedings of the 1978 National Conference on Control of Hazardous Material Spills, April 11-13, Miami Beach, Florida. pp. 315-324.

Hawthorne, H.S. 1982. Solvent Decontamination of PCB Electrical Equipment. In: IEEE Conference Record of the Industrial and Commercial Power Systems Technical Conference, Philadelphia, Pennsylvania, May 10-13, Institute of Electrical and Electronics Engineers, Inc., New York, New York, pp. 74-78.

Hedley, W.H., S.C. Cheng, B.O. Desai, C.S. Smith, and H.D. Toy. 1983. Alternate Treatment of Organic Solvents and Sludges from Metal Finishhing Operations: Final Report. NTIS Publication No. PB84-102151, EPA-600/52-83-094, U.S. Environmental Protection Agency, Cincinnati, Ohio. 363 pp.

Hennings, T.J., P.A. Painter, L.L. Scinto, and A.M. Takata. 1982. Preliminary Operations Plan and Guidelines for the At-Sea Incineration of Liquid PCB Wastes, NTIS Publication No. PB83-181834, EPA-600/52-82-068, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. 121 pp.

Herbst, E., et al. 1977. Fate of PCBs-^{14}C in Sewage Treatment--laboratory experiments with activated sludge. Chemosphere 6:725-730.

Hetling, L.J., T.J. Tofflemire, E.G. Horn, R. Thomas, and R. Mt. Pleasant. 1978. The Hudson River PCB Problem: Management Alternatives. Paper presented at the New York Academy of Sciences Conference on the Health Effects of Halogenated Aromatic Hydrocarbons, New York, New York, June 24-27, p. 630.

Hornig, A.W. 1984. Destruction of PCB-Contaminated Soils with a High-Temperature Fluid-Wall (HTFW) Reactor. In: Proceedings of the 1984 Hazardous Material Spills Conference: Prevention, Behavior, Control, and Cleanup of Spills and Waste Sites, Nashville, Tennessee, April 9-12, Government Institute, Rockville, Maryland, pp. 73-79.

Hornig, A.W. 1984. Destruction of PCB-Contaminated Soils with a High-Temperature Fluid-Wall (HTFW) Reactor. NTIS PB84-168798, EPA-600/D-84-072, U.S. Environmental Protection Agency, Cincinnati, Ohio. 23 pp.

Industrial Economics, Inc. 1985. Regulatory Analysis of Proposed Restrictions on Land Disposal of Certain Dioxin-Containing Wastes, Studies and Methods Branch, EPA, Washington, D.C.

Isbister, J.D., G.L. Anspach, and J.F. Kitchens. 1984. Composting for Degradation of PCBs in Soil. In: Proceedings of the 1984 Hazardous Materials Spills Conference: Prevention, Behavior, Control, and Cleanup of Spills and Waste Sites, Nashville, Tennessee, April 9-12, Government Institute, Rockville, Maryland, pp. 104-109.

Jenkins, T.F., D.C. Leggett, L.V. Parker, J.L. Oliphant, C.J. Martel, B.T. Foley, and C.J. Deiner. 1983. Assessment of the Treatability of Toxic Organics by Overland Flow. CREL 83-3, U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.

Kalmaz, E.V., R.B. Craig, and G.W. Zimmerman. 1981. Kinetics Model and Simulation of the Concentration Variations of the Species of Polychlorinated Biphenyls (PCBs) Involved in Photochemical Transformation. Preprint Extended Abstract. Presented before the Division of Environmental Chemistry at the 182nd Meeting of the American Chemical Society, New York, New York, August 23-28, 21(2):100-103.

Kitchens, J.F., G.L. Anspach, L.B. Mongoba, and E.A. Kobylinski. 1984. Cleanup of Spilled Chlorinated Organics with the LARC Process. In: Proceedings of the 1984 Hazardous Materials Spills Conference: Prevention, Behavior, Control, and Cleanup of Waste Sites, Nashville, Tennessee, April 9-12, Government Institute, Rockville, Maryland, pp. 110-115.

Kitchens, J.F., W.E. Jones, G.L. Anspach, and D.C. Schubert. 1982. Light-activated Reduction of Chemicals for Destruction of Polychlorinated Biphenyls in Oil and Soil. In: Symposium on the Detoxification of Hazardous Waste, Ann Arbor Science, Ann Arbor, Michigan, pp. 215-226.

Kluge, F.R., P.M. Balma, W. Turiansky, and R.V. Snow. 1982. PJM Joint Reactive Project Installation of 230 kV Shunt Capacitor Banks on the Public Service Electric and Gas Company System. Paper presented at the Pennsylvania Electric Association Fall Conference, Lancaster, Pennsylvania, September 14.

Kokoszka, L., and J. Flood. 1985. A Guide to EPA-Approved PCB Disposal Methods. Chem. Eng. pp. 41-43, July 8.

Komai, R.V. 1982. Current PCB Research. Presented before the Edison Electric Institute/Envirosphere Company 5th Annual Conference on Environmental Licensing and Regulatory Requirements Affecting the Electric Utility Industry, October 27-29, Washington, D.C. 13 pp.

Komai, R.Y., D.C. Van der Meer, J. Figler, M.A. Bender, R.P. Kale, M.S. Makar, and B.E. Pyatt. 1982. Current PCB Research. Paper presented at the 5th Conference of the Edison Electric Institute, Envirosphere Environmental Licensing, and the Electric Industry, Washington, DC, October 27-29.

Kong, H.L., and G.S. Sayler. 1983. Degradation and total mineralization of monohalogenated biphenyls in natural sediment and mixed bacterial cultures, Appl. Environ. Microbiol. 46:666-672.

Kopeoky, Anne L. 1985. PCB Biodegradation Using Sybron Bi-Chem 100b PB/Hudson River Isolates, Status Report. Sybron Chemicals, Birmingham, N.J.

Lacy, W.J., and R.G. Rice. 1977. The Status and Future of Ozone for Water and Wastewater Treatment. Ind. Water Eng. 14(5):14-19.

Lafornara, J.P. 1978. Cleanup After Spills of Toxic Substances. Water Pollut. Control Fed. J. 50(4):617-627.

Lahey, W., and M. Connor. 1983. The Case for Ocean Waste Disposal. Technol. Rev. 86(6):61-68.

Lapiere, R.B., et al. 1977. Catalytic Hydrochlorination of Polychlorinated Pesticides and Related Substances. Worcester Polytechnic Institute. Prepared for Municipal Environmental Research Lab. NTIS PB-262804.

Lauber, J.D. 1982. Burning Chemical Wastes as Fuels in Cement Kilns. J. Air Pollut. Control Assoc. 32(7):771-777.

Law Engineering Testing Company. 1982. Unsolicited Proposal for the Application of Ground Freezing Technology to Subsurface Contamination Control and Clean-up. Law Engineering Proposal No. 2032.91.

Lee, M.C., R.A. Griffin, M.L. Miller, and E.S.K. Chian. 1979. Adsorption of Water-Soluble Polychlorinated Biphenyl Aroclor 1242 and Used Capacitor Fluid by Soil Materials and Coal Chars. J. Environ. Sci. Health A14(5):415-442.

Ludwigson, J., ed. 1984. Proceedings of the 1984 Hazardous Material Spills Conference: Prevention, Behavior, Control and Cleanup of Spills and Waste Sites, Nashville, Tennessee, April 9-12. 445 pp.

MacCallum, A. D. 1948. A Dry Synthesis of Armoatic Sulfides: Phenylane Sulfide Resins. J. Org. Chem. 13:154-160.

March, J. 1968. Advanced Organic Chemistry. McGraw-Hill, New York.

Massey, M.J., and F.M. Walsh. 1985. An Electrochemical Process for Decontaminating PCB-Contaminated Transformer Coolants, EPRI, PCB Seminar. Seattle, Washington, October 22-25.

McCormick, D. 1985. One Bag's Meat. Biotechnology 3(May):429-435.

McGranaghan, M.F., and R.F. Gustin. 1982. Transient Switching Studies for EHV Shunt Capacitor Applications on the PJM System. Paper presented at the Pennsylvania Electric Association Fall Conference, Lancaster, Pennsylvania, September 14.

McGrath, M.F. 1980. The Fourth Coast. EPA J. 6(5):22-24.

McIntyre, A.E., R. Perry, and J.N. Lester. 1981. The Behavior of Polychlorinated Biphenyls and Organochlorine Insecticides in Primary Mechanical Wastewater Treatment. Environ. Pollut. (Series B) 21(3):223-233.

McManamon, K. 1982. Sunohio's PCBX Process. In: Minutes of the Meeting of the Pennsylvania Electric Association, Engineering Section Electrical Equipment Committee, Fall 1982, Lancaster, Pennsylvania, September 14-15, Pennsylvania Electric Association, Harrisburg, Pennsylvania. 9 pp.

Mercer, B.W., G.W. Dawson, J.A. McNeese, and E.G. Baker. 1984. Methods/Materials Matrix of Ultimate Disposal Techniques for Spilled Hazardous Materials. NTIS Publication No. PB85-116853, EPA-600/2-84-170, U.S. Environmental Protection Agency, Cincinnati, Ohio. 130 pp.

Merrick, N.J., L.L. Fox and D.M. Coker. 1983. Polychlorinated Biphenyl Removal by a Combined Industrial Sanitary Treatment Plant. In: Toxic and Hazardous Waste: Proceedings of the 15th Mid-Atlantic Industrial Waste Conference, Lewisburg, Pennsylvania, June 26-28, Butterworth Publishers, Boston, Massachusetts, pp. 402-415.

Meuser, J.M., and W.C. Weimer. 1982. Amine-Enhanced Photodegradation of Polychlorinated Biphenyls, Final Report. EPRI-CS-2513. Batelle Pacific Northwest Labs, Richland, Washington. U.S. Department of Energy, Washington, D.C. 61 pp.

Millan, R.C., and N.A. Ostenso. 1984. A Case Study of Storage and Disposal of PCB Contaminated Soils. In: Proceedings of the Conference on Hazardous Wastes and Environmental Emergencies: Management, Prevention, Cleanup, and Control. Hazardous Materials Control Research Institute, Silver Spring, Maryland, pp. 250-254.

Miller, R.A., and M.D. Sevientoniewski. (n.d) The Destruction of Various Organic Substances by a Catalyzed Wet Oxidation Process, Report for EPA, Contract 68-03-2568. Work Directive T-7016.

Miller, R.A., and R.D. Fox. 1982. Catalyzed Wet Oxidation of Hazardous Wastes from Detoxification of Hazardous Wastes. J.H. Exner, ed., Ann Arbor Science.

Modell, M., G.G. Gandet, M. Simson, G.T. Hong, and K. Blemen, 1982. Supercritical Water, Testing Reveals New Process Hold Promise, Solid Waste Management, August.

Monick, B., and A. Blake. 1983. New Industrial Wastewater Treatment Method for Removal of Multiple Contaminants. In: Proceedings of the 70th American Electroplaters Society Annual Technical Conference, Indianapolis, Indiana, June 27-30, American Electroplaters Society, Winter Park, Florida, 13 pp.

Muller, B.W., A.R. Brodd, and J.P. Leo. 1983. Hazardous Waste Remedial Action-Picillo Farm, Coventry, Rhode Island; An Overview. J. Hazard. Mater. 7(2):113-129.

Murakami, K., and K. Takeishi. 1976. Behvaior of Heavy Metals and PCB's in the Removal and Treatment Operations of Bottom Deposits. Paper presented at the Toxic Substances 2nd U.S./Japanese Experts Meeting, October 25-29.

National Institute for Occupational Safety and Health. 1977. NIOSH Criteria for a Recommended Standard Occupational Exposure to Polychlorinated Biphenyls (PCBs). DHEW (NIOSH) Publication No. 77-225, U.S. Department of Health, Education, and Welfare, Washington, DC. 224 pp.

New England River Basins Commission. 1980. Housatonic River Basin Overview. NTIS Publication No. PB82-107152, Water Resources Council, Washington, D.C. 209 pp.

New England River Basins Commission. 1980. Housatonic River Basin Overview. NTIS PB82-107152. Prepared for the Water Resources Council, Washington, D.C. 199 pp.

New York State Department of Environmental Conservation. 1985a. Status Report: PCB Biodegradation Using Sybron Bi-Chem 1006 PB/Hudson River Isolates. Office of Special Projects, Albany, New York, May 21. 2 pp.

New York State Department of Environmental Conservation. 1985b. Status Report: Wright-Malta Steam Gasification Process. Office of Special Projects, Albany, New York, May 17. 2 pp.

New York University. 1984. Development and Evaluation of a Low Energy Process Technology for Extraction and Chemical Destruction of Polychlorinated Biphenyls (PCB's) from Contaminated Soils and Sludges. NYU/DASP 84-02. New York, New York. 30 pp.

Oeschlaeger, H.F. 1976. Reactions of Ozone with Organic Compounds, Proc. Ozone Conference, Cincinnati, Ohio.

Pavlov, S.P., and W. Horn. 1978. PCB Removal from the Duwamish River Estuary: Implications to the Management Alternative for the Hudson River PCB Cleanup. Paper presented at the New York Academy of Sciences Conference on the Health Effects of Halogenated Aromatic Hydrocarbons, New York, New York, June 24-27, p. 651.

Peterson, R.C., A.S. Batolomeo, M.H. Corbin, and F. Roy. 1983. Lehigh Electric Site Superfund PCB Cleanup: Case History. In: 1983 National Conference on Environmental Engineering: Proceedings of the ASCE Specialty Conference, Boulder, Colorado, July 6-8, American Society of Chemical Engineers, New York, New York, pp. 766-774.

Peterson, S.A., and K.K. Randolph, eds. 1977. Management of Bottom Sediments Containing Toxic Substances: Proceedings of the Second U.S.-Japan Experts Meeting, October 1976, Tokyo, Japan. NTIS PB-272684, EPA-600/3-77-083, U.S. Environmental Protection Agency, Corvallis, Oregon. 303 pp.

Peterson, R., and E. Milicic. 1985. Chemical Destruction/Detoxification of Chlorinated Dioxins in Contaminated Soils, Summary Report (10-84--5-85, sponsored by EPA and Air Force E.56), Galson Research Corporation, E. Syracuse, New York.

Plimmer, J.R. 1978. Approaches to Decontamination or Disposal of Pesticides: Photodecomposition. ACS Symposium Series, No. 73, American Chemical Society, Washington, DC, p. 13.

Prengle, H.W., and C.E. Mauk. 1978. New technology: Ozone/UV chemical oxidation wastewater process for metal complexes, organics, and disinfection, AICHE Symp. Series 7:228-243.

Rhee, G-Y. 1985a. Anaerobic Biodegradation of PCBs in Hudson River Sediments and Dredged Sediment Disposal Sites. Proposal submitted to the New York State Department of Environmental Conservation, Albany, New York. 13 pp.

Rhee, G-Y. 1985b. Letter to R. Mt. Pleasant, May 16.

Rhee, G-Y, M. Chen, and B. Bush. 1985. Anaerobic Biodegradation of PCBs. Proposal submitted to the New York State Department of Environmental Conservation, Albany, New York. 17 pp.

Rochkind, M.L., G.S. Saylor, and J.W. Blackburn. 1985. Microbial Decomposition of Chlorinated Hydrocarbons, EPA Contract 68-03-3074-3.

Rogers, C. J., and A. Kornel. 1985. Laboratory and Field Tests of Chemical Reagents for In-Situ Dextoxification of Chlorinated Dioxins in Soils. Paper presented at the American Chemical Society National Meeting, Chicago, Illinois, September.

Rogers, C.J. 1983. Chemical Treatment of PCBs in the Environment In: Proceedings of the 8th Annual Research Symposium. Fort Mitchell, Kentucky, March 8-10, 1982, EPA-600/9-83-003, U.S. Environmental Protection Agency, pp. 197-201.

Rogers, C.J. 1985. Letter to J.B. White, July 19.

Ruzz, B., M. Iqbal, W. Brenner, and C.J. Rogers. 1985. A Low Energy Process for the Extraction and Chemical Destruction of PCBs from Contaminated Soils and Sludges. Paper presented at the American Chemical Society National Meeting, Chicago, Illinois, September.

Saunders, M.B. 1985. Pilot Studies for Solvent Extraction of PCB from Soil, EPRI PCB Seminar, Seattle, Washington. October 22-25.

Schact, R.A. 1974. Pesticides in the Illinois Waters of Lake Michigan. NTIS PB-245150, EPA 600/3-74-002, U.S. Environmental Protection Agency. Washington, D.C. 55 pp.

Schiaris, M.P., and G.S. Saylor. 1982. Biotransformation of PCB by Natural Assemblages of Freshwater Microorganisms. Environ. Sci. & Tech., 16:367-369.

Scholz, R., and J. Milanowski. 1984. EPA Project Summary: Mobile System for Extracting Spilled Hazardous Materials from Excavated Soils. J. Hazard. Mater. 91(2):241-252.

Schwinn, D.E., D.F. Storrier, R.J. Moore, and W.S. Carter. 1984. PCB Removal by Carbon Adsorption. Pollut. Eng. 16(1):20-21.

Shen, T.T. 1982. Estimation of Organic Compound Emissions from Waste Lagoons. J. Air Pollut. Control Assoc. 32(1):79-82.

Sloan, K.J., et al. 1983. Temporal Trends Toward Stability of Hudson River PCB Decontamination, Bull. Envir. Contam. Toxicol., 31:377-385.

Smith, J.G., and L.B. Gurbacham. 1981. The Use of Sodium Naphthalenide to Chemically Destroy Polychlorinated Biphenyl by Dechlorination. Preprint Extended Abstract. Presented before the Division of Environmental Chemistry at the 182nd Meeting of the American Chemical Society, New York, New York, August 23-28, 21(2):88-89.

Snell Environmental Group, Inc. 1982. Rate of Biodegradation of Toxic Organic Compounds While in Contact with Organics Which Are Actively Composting: 1982 Final Report. NTIS Publication No. PB84-193150, National Science Foundation, Washington, DC.

Sonksen, M.K., and J.A. Lease. 1983. Evaluation of Cement Dust Stabilization of Polychlorinated Biphenyl-Contaminated Sludges. In: Proceedings of the 37th Industrial Waste Conference, Purdue University, West Lafayette, Indiana, May 11-13, Ann Arbor Sicence, Ann Arbor, Michigan, pp. 405-412.

Spittler, T.M. 1984. Field Measurement of Polychlorinated Biphenyls in Soil and Sediment Using a Portable Gas Chromatograph. ACS Symposium Series, American Chemical Society, Washington, DC, 267:37-42.

Star, R. 1977. The Development of Pollution Control in Japan. IV. American and Japanese Controls of Polychlorinated Biphenyls (PCBs). Harv. Environ. Law Rev. 1:561-567.

Strek, H.J. 1980. Factors Affecting the Bioavailability of Polychlorinated Biphenyls (PCBs) in Soils. NTIS PB81-209223, Prepared for the Office of Water Research and Technology, Washington, D.C. 109 pp.

Strek, H.J., J.B. Weber, P.J. Shea, E. Mrozek, and M.R. Overcash. 1981. Reduction of Polychlorinated Biphenyl Toxicity and Uptake of Carbon-14 Activity by Plants Through the Use of Activated Carbon. J. Agric. Food Chem. 29(2):288-293.

Stretz, L.A., L.C. Borduin, W.E. Draper, R.A. Koenig, and J.S. Vavruska. 1982. Controlled Air Incineration of Hazardous Chemical Waste at the Los Alamos National Laboratory. In: Proceedings of the 1982 Symposium on Waste Management: Waste Isolation in the U.S. and Elsewhere, Technical Programs and Public Communications. Vol. 1: General, Tucson, Arizona, March 8-11, Arizona Board of Regents, Tucson, Arizona, pp. 281-299.

Stroud, F.B., R.T. Wilkerson, and A. Smith. 1978. Treatment and Stabilization of PCB Contaminated Water and Waste Oil: A Case Study. In: Proceedings of the 1978 National Conference on Control of Hazardous Material Spills, Miami Beach, Florida, April 11-13, Information Transfer, Rockville, Maryland, pp. 135-144.

Subnamanian, R.V., and R. Mahalingam. 1977. Immobilization of Hazardous Residuals by Encapsulation (Semi-Annual Technical Report). NTIS PB-271410. National Science Foundation, Washington, D.C. 93 pp.

Sunohio. (n.d.) PCBX: Chemical Destruction of PCB's. Brochure. Sunohio, 1700 Gateway Boulevard, SE, Canton, Ohio 47707.

Sweeny, K.H., and J.R. Fischer. 1970. Investigation of Means for Controlled Self-Destruction of Pesticides. NTIS Publication No. PB-198224. U.S. Environmental Protection Agency, Washington, DC. 131 pp.

Sworzen, E.M., and D.G. Ackerman. 1982. Interium Guidelines for the Disposal/ Destruction of PCBs and PCB Items by Non-thermal Methods. NTIS Publication No. PB82-217498, EPA-600/2-82-069, U.S. Environmental Protection Agency, Washington, DC.

Taylor, D. 1984. Managing Organics in Sludge Reuse Programs. BioCycle 25(6):20-22.

Thomason, T.B. and M. Modell, 1984. Supercritical Water Destruction of Aqueous Wastes, Hazardous Waste 1(4):453-467.

Thorneloe, S. 1986. EPA/OAQPS. Land Treatment Data Base, Memorandum to J. Durham, January 31.

Timmerman, C.L. 1985. In Situ Vitrification of PCB-Contaminated Soils, EPRI PCB Seminar, Seattle, Washington, October 22-25.

Tittlebaum, M.E., et al. 1985. "State of the Art on Stabilization of Hazardous Organic Liquid Wastes and Sludges." CRC Critical Reviews in Environmental Control, Vol. 15, Issue 2, pp. 179-211.

Trump, J.G., K.A. Wright, A.J. Sinskey, D.N. Shan, and R. Fernald. 1979. Disinfection of Municipal Sludge and Wastewater by Energized Electrons. Report No. INIS-MF-6718, In: Proceedings of the International Seminar on Radioisotopes and Radiation Applied to Environmental Protection, Sao Paulo, Brazil, September 17.

Tucker, E.S., et al. 1975. Activated sludge primary biodegradation of PCB's. Bull. Environ. Contam. Toxicol. 14:705-713.

Tulp, M.T.M., R. Schmitz, and O. Hutzinger. 1978. The Bacterial Metabolism of 4,4'-Dichlorobiphenyl and Its Suppression by Alternative Carbon Sources. Chemosphere 7(1):103-108.

U.S. Army Corps of Engineers, Water Resources Support Center. 1983. Management of Bottom Sediments Containing Toxic Substances: Proceedings of the 7th U.S./Japan Experts Meeting, November 2-4, 1981, New York, New York. Cont. Accession No. A136740. 421 pp.

U.S. Environmental Protection Agency. 1980. Identification and Listing of Hazardous Waste. 40 CFR 261, Final regulation, Federal Register.

U.S. Environmental Protection Agency. 1980. Polychlorinated Biphenyls (PCBs) in Manufacturing, Processing, Distribution in Commerce, and Use Prohibition. 40 CFR 761, Final regulation, Federal Register.

U.S. Environmental Protection Agency. 1985. Assessment of Incinerators as a Treatment Method for Liquid Organic Hazardous Wastes: Summary and Conclusions. Washington, DC, March. 5 pp.

U.S. Environmental Protection Agency, and Oil Spill Control Association of America. 1978. Control of Hazardous Material Spills: Proceedings of the 1978 National Conference in Control of Hazardous Material Spills, Miami Beach, Florida, April 11-13. 458 pp.

United States Patent Office. 1983. Method and Apparatus for Treating Polychlorinated Biphenyl Contaminated Sludge. U.S. Patent No. 4,402,274, Issued to W.C. Meenan and G.D. Sullivan, September 6.

United States Patent Office. 1984a. Destruction of Polychlorinated Biphenyls and Other Hazardous Halogenated Hydrocarbons, U.S. Patent No. 4,469,661, Issued to C.E. Shultz, September 4.

United States Patent Office. 1984b. Methods for Decontaminating Soil. U.S. Patent No. 4,447,541, Issued to R.L. Peterson, May 8.

Unterman, R., et al. 1985. Microbial Degradation of Polychlorinated Biphenyls, Proceedings of Tenth Conf. on New Frontiers for Hazardous Waste Management, Pittsburgh, Pennsylvania. September 15-18. EPA/600-9-85-025.

v. Löw, E. 1983. Vorkommen und Mikrobieller Umund Abbau von aromatischen Polyzyklen im Boden und in Siedlungsabfällen. Forum Städte-Hygiene 34(5):263-267.

V. Meyer, W. C. 1986. A Study of Thionation Reactions for Use in Destruction of Toxic Wastes, Initial Tests of Thionation Reaction Conditions with Priority Pollutants. Fairview Industries, Inc., Middleton, Wisconsin July. EPA Contract No. 68-02-3992.

Versar, Inc. 1976. Assessment of Wastewater Management, Treatment, Technology, and Associated Costs for Abatement of PCB Concentrations in Industrial Influents.

Versar, Inc. 1984. Work Plan for PCB Analyses. Versar Proposal No. 84-989. Submitted to the New York State Department of Environmental Conservation, Albany, New York, June 28.

Walker, K.H. 1977. The Great Lakes Cleanup. Water: Sewage Works 124(11):85.

Weaver, G. 1982. PCB Pollution in the New Bedford, Massachusetts Area: A Status Report. Massachusetts Office of Coastal Zone Management, Report submitted to the Massachusetts New Bedford PCB Task Force, June. 62 pp.

Webber, M.D., H.D. Monteith, and D.G.M. Corneau. 1981. Assessment of Heavy Metals and PCB's at Selected Sludge Application Sites in Ontario. Research Report No. 109, Research Program for the Abatement of Municipal Pollution Under the Provisions of the Canada-Ontario Agreement on Great Lakes Water Quality, Environment Canada, Environmental Protection Service, Ottawa, Ontario. 27 pp.

Weitzman, L. 1981. Treatment and Destruction of PCB and PCB Contaminated Materials. Preprint Extended Abstract. Presented before the Division of Environmental Chemistry at the 182nd Meeting of the American Chemical Society, New York, New York, August 23-28, 21:42-44.

Weitzman, L. 1984. Cleaning of PCB Contaminated Soils, Proceedings of 1983 PCB Seminar, EPRI, Atlanta, Georgia. December 6-8.

Weitzman, L. 1985. Solvent Cleaning of PCB Contaminated Soils, PCB Seminar EPRI, Seattle, Washington, October 22-25.

West, P.R., S.K. Chaudhary, and R.H. Mitchell. 1983. Photodechlorination of Polychlorinated Biphenyls Induced by Hydroquinone in Basic Media. Presented before the Division of Environmental Chemistry at the 186th Meeting of the American Chemical Society, Washington, DC, August 28-September 2, 23(2):384-387.

West, R.H., and P.G. Hatcher. 1980. Polychlorinated Biphenyls in Sewage Sludge and Sediments of the New York Bight. Marine Pollut. B. (11):126-129.

White, J.B. 1985. Technical/Economic Assessment of Selected PCB Sediment Decontamination Processes: Work Plan. Prepared by Research Triangle Institute for the U.S. Environmental Protection Agency Under Contract No. 68-02-3992, Work Assignment 26, Research Triangle Park, North Carolina. 7 pp.

Whitmore, F.C., and J.D. Barden. 1983. A Study of PCB Destruction Efficiency and Performance for a Coal-Fired Utility Boiler. Vol. 1 and 2. NTIS Publication Nos. PB84-110147 and PB84-110154, EPA-600/52-83-101a and b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. 79 pp.

Young, D.R., and T.C. Heeson. 1977. Polychlorinated Biphenyls in the Near-shore Marine Ecosystem off San Diego, California. Report No. SCCWRP-109, Prepared by the Southern California Coastal Water Research Project for the California Regional Water Quality Board, San Diego, California. NTIS PB-283090, 21 pp.

Young, D.R., D. McDermott-Erlich, and T.C. Heesoon. 1977. Sediments as Sources of DDT and PCB. Marine Pollut. Bull. 8(11):254-257.

Zimmie, T.F., and T.J. Tofflemire. 1978. Maintenance Dredging and Toxic Substances. In: Proceedings of the 2nd Conference on International Waterborne Transport. ASCE Urban Transportation Division Specialty Conference, New York, New York, October 5-7, 1977, American Society of Chemical Engineers, New York, New York, pp. 704-719.